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FOR 2024 EXAM

CBSE 10 SOLVED PAPERS

2023-2014 YEARS

CHAPTERWISE-TOPICWISE

- TERM I, TERM II, DELHI, ALL INDIA, FOREIGN & COMPARTMENT PAPERS
- LAST 3 YEARS CBSE OFFICIAL SAMPLE QUESTIONS
- ANSWERS AS PER CBSE MARKING SCHEME WITH PREPARATORY TOOLS AND TOPPER'S ANSWERS

CLASS 12

- Topicwise Graphical Analysis • Comprehensive Theory with Brain Map
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CHEMISTRY

CBSE 10 SOLVED PAPERS
2023-2014 YEARS

CHAPTERWISE-TOPICWISE

CHEMISTRY

CLASS 12

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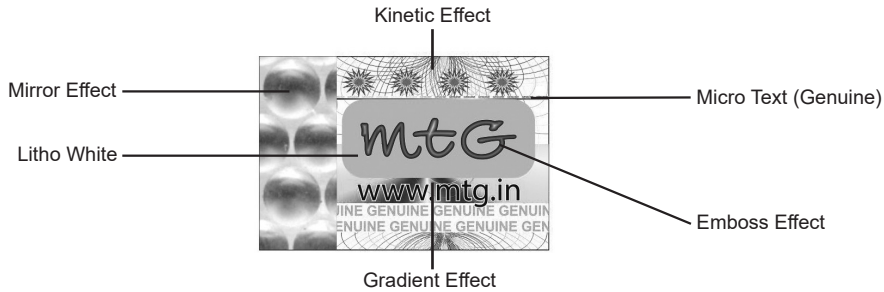


Preface

We feel pleased and delighted in presenting the revised edition of the book **"CBSE Champion Chapterwise-Topicwise Chemistry"** as per the CBSE Curriculum for the current academic year. As we know, CBSE Board has taken multiple steps towards the implementation of Competency Based Education (CBE) in schools, range from aligning assessment to CBE, development of exemplar resources for teachers and students on CBE pedagogy and assessment and continued teacher capacity building so, special efforts have been put to align this book to CBE. It will give students comprehensive knowledge of subject according to the latest CBSE syllabus and pattern.

The salient features of the book are as follows :

- **Topicwise Graphical Analysis :** Bar Graph Analysis of Previous 10 Years' CBSE Board Papers' Questions (MCQ, 1 mark, 2 marks, 3 marks, 5 marks) is provided. The Graph and 'Weightage Xtract' will help students to figure out the chapters and topics which are to be revised frequently and how much is the weightage of these topics.
- **Comprehensive and Lucid Theory :** Well explained theory with important formulae, flowcharts and tables for quick recap and summarise the chapter with Brain Map.
- **Chapterwise-Topicwise Questions and Solutions :** Previous 10 years' CBSE-Term I, Term II, DELHI, ALL INDIA and FOREIGN papers' questions are segregated chapterwise-topicwise. Detailed solutions of these questions are also given according to the CBSE Marking Scheme.
- **Strictly Based on CBSE Syllabus & NCERT Topics List :** Topicwise questions are arranged in descending chronological (2023-2014) order, so that latest years' questions come first in practice and revision. In the previous years' CBSE papers SA I, SA II and LA type questions are generally framed by clubbing together questions from different topics and chapters. These questions are segregated strictly according to NCERT topics. *e.g.*, (1/3, Delhi 2016), this question of 1 mark was asked in SA II type category, (1/5, AI 2015), this question of 1 mark was asked in LA type category, (1/2, Foreign 2016), this question of 1 mark was asked in SA I type category.
- **CBSE Cognitive Levels :** Questions are labelled as per the cognitive levels issued by CBSE for assessment and evaluation to provide evidence of students' knowledge and ability.

Cognitive Levels :

Remembering	Understanding	Applying	Analysing	Evaluating	Creating
R	U	Ap	An	Ev	Cr

- **Key Concepts Highlight :** Key concepts have been highlighted in the solutions for their reinforcement.
- **Exam Preparatory Tools :** Detailed solutions are supplemented with Exam Preparatory Tools like **Key Points, Answer Tips, Concept Applied, Commonly Made Mistakes, Alternative Methods, Shortcuts,** etc. to improve aspirant's score.
- **Topper's Answers :** Topper's Answers of few selected CBSE-2022 Questions are given which will help aspirants to write perfect answers in the upcoming CBSE Board Exam.
- **Chapterwise Self Assessments (Solved) :** To master a chapter, self assessment test is given at the end of each chapter, covering all typology of questions.
- **CBSE Sample Questions :** Last three years' official CBSE Sample Questions are segregated chapterwise-topicwise for which solutions are given as per the CBSE Marking Scheme.
- **Practice Papers as per the Latest Syllabus :** 5 Practice Papers (Solved) strictly based on the latest syllabus, latest design and blueprint of CBSE Sample Paper issued by CBSE Board. Various types of questions like Case/Passage/Source Based Questions, MCQ, Assertion-Reason, SA and LA type are included.
- **Solved CBSE Sample Paper :** Latest solved CBSE sample paper is included.

We are sure that the value addition done in this revised book will be helpful to students in achieving success in the coming board examinations. Every possible effort has been made to make this book error free. Useful suggestions by our readers for the rectification and improvement of the book content would be gracefully acknowledged and incorporated in further editions.

Readers are welcome to send their suggestions and feedback at **editor@mtg.in**.

All the Best

MTG Editorial Board

Glimpse of MTG CBSE Champion

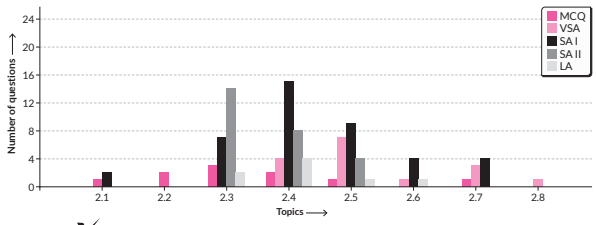
CHAPTER 2

Electrochemistry

TOPICS

2.1 Electrochemical Cells
2.2 Galvanic Cells
2.3 Nernst Equation
2.4 Conductance of Electrolytic Solutions
2.5 Electrolytic Cells and Electrolysis
2.6 Batteries
2.7 Fuel Cells
2.8 Corrosion

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topics 2.3 *Nernst Equation* and 2.4 *Conductance of Electrolytic Solutions* are highly scoring topics.
- Maximum VSA, SA I type questions were asked from Topics 2.3, 2.4 and 2.5 *Nernst Equation, Conductance of Electrolytic Solutions* and *Electrolytic Cells and Electrolysis*.
- Maximum SA II and LA type questions were asked from Topic 2.3 *Nernst Equation*.

Helps you to figure out the topics which carry maximum weightage!

QUICK RECAP

- **Chemical kinetics :** It is the branch of chemistry which deals with the study of reaction rates and their mechanisms.
- **Rate of a reaction :** The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time. For the reaction,

$R \longrightarrow P$, Rate $= -\frac{\Delta[R]}{\Delta t}$ or $+\frac{\Delta[P]}{\Delta t}$

- **Units of rate :** Concentration time^{-1} *i.e.*, mol L^{-1} s^{-1} or atm s^{-1} for gaseous reactions.
- **Average rate of reaction :** The rate of change in concentration of any reactant or product during a large time interval.

$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$

BRAIN MAP

SOLUTIONS

A solution is a homogeneous mixture of two or more substances whose composition can be varied with certain limits. The component of solution present in larger quantity is called solvent while the component present in lesser quantity is called solute.

Composition of Solutions : Expressing Concentration of Solution

Mass percentage : Mass % of the solution = $\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$

Parts per million : ppm of A = $\frac{\text{Mass of component } A}{\text{Total mass of solution}} \times 10^6$

Molarity : Molarity (M) = $\frac{\text{Moles of solute}}{\text{Volume of solution (mL)}} \times 1000$

Molality : Molality (m) = $\frac{\text{Moles of solute}}{\text{Mass of solvent in grams}} \times 1000$

Mole Fraction : Mole fraction of a component = $\frac{\text{No. of moles of the component}}{\text{Total no. of moles of all component}}$

Normality : Normality (N) = $\frac{\text{No. of gram equivalent of solute}}{\text{Volume of solution in mL}} \times 1000$

Formality : Formality (F) = $\frac{\text{No. of formula masses of solute}}{\text{Volume of solution in litre}}$

Laws

Henry's Law : The law states that "the mass of a gas (m) dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure (p) the gas in equilibrium with the solution."
$m \propto p$; $m = K_H p$
$x_A = K_H p$
where,
K_H = Henry's constant

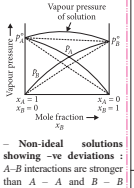
Raoult's Law : The law states that "at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component in solution is equal to the product of the vapour pressure of pure component and its mole fraction".
$P_A = p_A^\circ \times x_A$; $P_B = p_B^\circ \times x_B$

Types of Solution

Ideal solutions : $A - B$ interactions are of same magnitude as $A - A$ and $B - B$ interactions, $\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$.

Non-ideal solutions : $A - B$ interactions are of different magnitude than $A - A$ and $B - B$ interactions, $\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$.

– **Non-ideal solutions showing +ve deviations :** $A - B$ interactions are weaker than $A - A$ and $B - B$ interactions, ΔV_{mix} = +ve, ΔH_{mix} = +ve and resulting vapour pressure is higher than that expected.



– **Non-ideal solutions showing –ve deviations :** A–B interactions are stronger than $A - A$ and $B - B$ interactions, ΔV_{mix} = –ve, ΔH_{mix} = –ve and resulting

Colligative Properties

Relative lowering in vapour pressure : The relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute (X_B) at a given temperature.
$\frac{P_A^\circ - P_A}{P_A^\circ} = X_B$

Elevation in boiling point : Elevation in boiling point (*i.e.*, ΔT_b) is directly proportional to the molality (m) of the solute in solution.
$\Delta T_b \propto m$
$\Delta T_b = K_b m$
where,
K_b = molal boiling point elevation constant.

Depression in freezing point : Depression in freezing point (*i.e.*, ΔT_f) is directly proportional to the molal concentration of solute (m).
$\Delta T_f \propto m$
$\Delta T_f = K_f m$

Quickly revise chapter from 'Quick Recap' and summarise through 'Brain Map'!

Previous Years' CBSE Board Questions

6.1 Classification

MCQ

1. Which one of the following halides contains C_{sp^2} — X bond?
(a) Allyl halide (b) Alkyl halide
(c) Benzyl halide (d) Vinyl halide
(Term I, 2021-22) Ap

VSA (1 mark)

2. Out of and , which is an example of allylic halide? *(AI 2017)*

3. Out of and , which is an example of vinylic halide? *(AI 2017)*

4. Out of and , which is an example of a benzylic halide? *(AI 2017)* U

6.2 Nomenclature

VSA (1 mark)

5. Write the IUPAC name of $CH_3CH=CH-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$
(AI 2019, Delhi 2013)

6. Write the structure of 1-bromo-4-chlorobut-2-ene. *(Delhi 2017)*

7. Write the structure of 3-bromo-2-methylprop- 1-ene. *(Delhi 2017)* U

8. Draw the structure of 2-bromopentane. *(Delhi 2014C)*

6.4 Methods of Preparation of Haloalkanes

MCQ

11. The synthesis of alkyl flouride is best obtained from
(a) Free radicals (b) Swarts reaction
(c) Sandmeyer reaction (d) Finkelstein reaction.
(2023)

12. Which of the following isomer of pentane (C_5H_{12}) will give three isomeric monochlorides on photochemical chlorination?
(a) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (b) $CH_3CH_2CH_2CH_2CH_3$
(c) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$ (d) All of the above.
(Term I, 2021-22) An

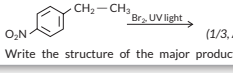
VSA (1 mark)

13. How can you convert the following?
But-1-ene to 1-iodobutane *(NCERT, 1/3, 2020)* An

14. Give reason for the following:
Thionyl chloride method is preferred for preparing alkyl chloride from alcohols. *(1/3, AI 2019)* U

15. Write equation for preparation of 1-iodobutane from 1-chlorobutane. *(1/3, AI 2019)*

16. How do you convert:
Propene to 1-iodopropane? *(1/3, AI 2016)*

17. Write the major product in the following:

(1/3, AI 2016)

18. Write the structure of the major product in the

Chapterwise-Topicwise last 10 years' question papers with CBSE cognitive levels labelling!

Last 3 years' CBSE sample questions are segregated sectionwise/chapterwise with CBSE cognitive levels labelling!

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. (c): $[Co(NH_3)_5SO_4]Cl \xrightarrow{AgNO_3} \underset{\text{(white ppt)}}{AgCl\downarrow}$

Only Cl^- ion gets ionise, SO_4^{2-} will not ionise since it is present inside coordination sphere.

2. (a): For one mole of the compound, two moles of AgCl are precipitated which indicates two ionisable chloride ions in the complex. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$

3. For one mole of the compound, two moles of AgCl are precipitated which indicates two ionisable chloride ions in the complex. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$

7. (c): $C_2O_4^{2-}$ is a chelating ligand, it forms a chelate complex with metal ion.

8. (a): The coordination number of Cr in $[CrCl_2(ox)_2]^{3-}$ is 6 as Cl is monodentate ligand and oxalate is bidentate ligand.

9. (b): Ethane-1, 2-diamine (*en*) is a bidentate ligand.

Key Points

- The secondary valency is equal to the coordination number.

10. (d): Formation of chelate rings increases the stability of the complex.

11. (a): As CO is a neutral ligand, its oxidation state is zero. The oxidation state of Ni in $Ni(CO)_4$ is calculated as follows :

$x + 4(0) = 0, x = 0$

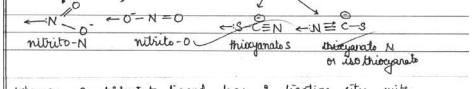
28.

(i) $[Co(NH_3)_4(H_2O)Cl]Cl_2$

Tetraammine Aqua chloride Cobalt (III) Chloride

(ii) An ambidentate ligand has 2 ligating atoms out of which at a time only one bonds with the central metal atom

Eg : NO_2^- (Nitrite) SCN^- (thiocyanate)



whereas a bidentate ligand has 2 ligating sites with which it simultaneously bonds to central metal atom

Eg : oxalate and ethane 1,2 diamine

$(C_2O_4)^{2-}$ COO^- COO^- $H_2N-CH_2-CH_2-NH_2$

(iii) Although ammonia is a strong field ligand but out of $[Fe(NH_3)_6]^{+3}$ and $[Fe(C_2O_4)_3]^{-3}$; $[Fe(C_2O_4)_3]^{-3}$ is more stable because oxalate is a bidentate ligand and therefore forms a chelating complex which provides it more stability as compared to the unidentated complex of similar structure.

$\therefore [Fe(C_2O_4)_3]^{-3} > [Fe(NH_3)_6]^{+3}$ in stability

[Topper's Answer, 2022]

Completely solved chapterwise self assessments and practice papers (based on the latest CBSE Sample Paper), covering all typology of questions which help to decode the CBSE exam pattern!

CBSE SAMPLE PAPER 2023-24

(Based on CBSE Circular released on 31st March 2023)

General Instructions :
Read the following instructions carefully.
(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple -choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case - based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION - A

The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Which of the following solutions will have the highest conductivity at 298 K?
(a) 0.01 M HCl solution
(b) 0.1 M HCl solution
(c) 0.01 M CH_3COOH solution
(d) 0.1 M CH_3COOH solution

(b) The carbon-magnesium bond is covalent and non-polar in nature.
(c) During S_N1 reaction, the carbocation formed in the slow step being sp^2 hybridised is planar.
(d) Out of $CH_2{=}CH{-}Cl$ and $C_6H_5CH_2Cl$, $C_6H_5CH_2Cl$ is more reactive towards S_N1 reaction.

6. Match the properties with the elements of 3*d* series:
(i) Lowest enthalpy of atomisation (p) Sc
(ii) Shows maximum number of oxidation states (q) Mn

CBSE Sample Questions

2.3 Nernst Equation

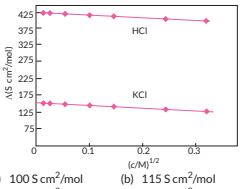
SA II (3 marks)

1. Represent the cell in which the following reaction takes place. The value of $E°$ for the cell is 1.260 V. What is the value of E_{cell}?
$2Al_{(s)} + 3Cd^{2+}(0.1\,M) \rightarrow 3Cd_{(s)} + 2Al^{3+}(0.01\,M)$
(Term II, 2021-22)

2.4 Conductance of Electrolytic Solutions

MCQ

2. The molar conductivity of CH_3COOH at infinite dilution is 390 $S\,cm^2$/mol. Using the graph and given information, the molar conductivity of CH_3COOK will be



(a) 100 $S\,cm^2$/mol (b) 115 $S\,cm^2$/mol
(c) 150 $S\,cm^2$/mol (d) 125 $S\,cm^2$/mol
(Term-II, 2021-22)

S.No.	Ions	Limiting molar conductivity / $S\,cm^2\,mol^{-1}$
1.	H^+	349.6
2.	Na^+	50.1
3.	K^+	73.5
4.	OH^-	199.1

(a) 350 $S\,cm^2\,mol^{-1}$ (b) 375.3 $S\,cm^2\,mol^{-1}$
(c) 390.5 $S\,cm^2\,mol^{-1}$ (d) 340.4 $S\,cm^2\,mol^{-1}$
(2020-21) An

SA I (2 marks)

4. Solutions of two electrolytes 'A' and 'B' are diluted. The Λ_m of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte? Justify your answer. Graphically show the behaviour of 'A' and 'B'. *(Term II, 2021-22)*

LA (5 marks)

5. (i) State Kohlrausch law.
(ii) Calculate the emf of the following cell at 298 K :
$Al_{(s)}|Al^{3+}(0.15\,M)\,||\,Cu^{2+}(0.025\,M)\,|\,Cu_{(s)}$
(Given $E°_{(Al^{3+}/Al)} = -1.66$ V, $E°_{(Cu^{2+}/Cu)} = 0.34$ V, $\log 0.15 = -0.8239$, $\log 0.025 = -1.6020$)
(2020-21)

6. (i) On the basis of $E°$ values identify which amongst the following is the strongest oxidising agent?
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-$; $E° = +1.36$ V,
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$; $E° = +1.51$ V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$;

Detailed solutions are supplemented with Exam Preparatory Tools like Key Points, Answer Tips, Concept Applied, Commonly Made Mistakes, Alternative Methods, Shortcuts, Topper's Answers, etc. to improve aspirants score!

Self Assessment

Case Based Questions (5 marks)

1. **Read the passage given below and answer the following questions :**
According to the collision theory for a chemical reaction to occur there must be collisions among the reactant molecules. However most of the collisions taking place among the reactant molecules are ineffective, only those collisions result in chemical

(a) is always less than E_a
(b) can be less than or more than E_a
(c) is always double of E_a
(d) is negative of E_a.

(v) It has been found that for a chemical reaction with rise in temperature by 10°C, the rate constant is
(a) nearly doubled (b) nearly tripled
(c) increases 5 times (d) increases 4 times.

PRACTICE PAPER 1

General Instructions :
Read the following instructions carefully.
(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple - choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case - based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. $\Lambda°$ ($ClCH_2COONa$) = 224 ohm^{-1} cm^2 mol^{-1}, $\Lambda°$(NaCl) = 38.2 ohm^{-1} cm^2 mol^{-1}, $\Lambda°$(HCl) = 203 ohm^{-1} cm^2 mol^{-1}, what is the value of $\Lambda°$($ClCH_2COOH$)?
(a) 288.5 ohm^{-1} cm^2 mol^{-1}
(b) 289.5 ohm^{-1} cm^2 mol^{-1}
(c) 388.8 ohm^{-1} cm^2 mol^{-1}
(d) 59.5 ohm^{-1} cm^2 mol^{-1}

6. Which of the following ions are coloured ?
1. Cu^+ 2. Ti^{4+}
3. Co^{2+} 4. Fe^{2+}
(a) 1, 2, 3, 4 (b) 3, 4
(c) 2, 3 (d) 1, 2

7. The rate of the reaction, $A + B + C \longrightarrow P$ is given by :
$r = -\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/2}[C]^{1/4}$.
The order of the reaction is
(a) 1 (b) 2 (c) 1/2 (d) 5/4

8. The most basic amine among the following is

Latest CBSE Sample Paper has been included.

Syllabus*

CLASS - XII (2023-24)

(THEORY)

Time : 3 Hours **Marks :** 70

S. No.	Unit	Periods	Marks
1	Solutions	10	7
2	Electrochemistry	12	9
3	Chemical Kinetics	10	7
4	*d*- and *f*-Block Elements	12	7
5	Coordination Compounds	12	7
6	Haloalkanes and Haloarenes	10	6
7	Alcohols, Phenols and Ethers	10	6
8	Aldehydes, Ketones and Carboxylic Acids	10	8
9	Amines	10	6
10	Biomolecules	12	7
	Total		**70**

Unit II : Solutions **10 Periods**

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, van't Hoff factor.

Unit III : Electrochemistry **12 Periods**

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.

Unit IV : Chemical Kinetics **10 Periods**

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit VIII : *d*- and *f*- Block Elements **12 Periods**

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

Lanthanoids : Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences.

Actinoids : Electronic configuration, oxidation states and comparison with lanthanoids.

Unit IX : Coordination Compounds **12 Periods**

Coordination compounds : Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, the

**For latest details refer www.cbse.gov.in*

importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit X : Haloalkanes and Haloarenes. 10 Periods

Haloalkanes : Nomenclature, nature of C–*X* bond, physical and chemical properties, optical rotation mechanism of substitution reactions.

Haloarenes : Nature of C–*X* bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit XI : Alcohols, Phenols and Ethers 10 Periods

Alcohols : Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

Phenols : Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

Ethers : Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit XII : Aldehydes, Ketones and Carboxylic Acids 10 Periods

Aldehydes and Ketones : Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.

Carboxylic Acids : Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

Unit XIII : Amines 10 Periods

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Diazonium salts : Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit XIV : Biomolecules 12 Periods

Carbohydrates : Classification (aldoses and ketoses), monosaccharides (glucose and fructose), *D*-*L* configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates.

Proteins : Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure.

Vitamins : Classification and functions.

Nucleic Acids : DNA and RNA.

QUESTION PAPER DESIGN

CLASS - XII (2023-24)

Subject : Chemistry

Theory (70 Marks)

S.No.	Domains	Marks	%
1.	**Remembering and Understanding :** Exhibit memory of previously learned material by recalling facts, terms, basic concepts and answers. Demonstrate understanding of facts and ideas by organizing, comparing, translating, interpreting, giving descriptions and stating main ideas.	28	40
2.	**Applying :** Solve problems to new situations by applying acquired knowledge, facts, techniques and rules in a different way.	21	30
3.	**Analyzing, Evaluating and Creating :** Examine and break information into parts by identifying motives or causes. Make inferences and find evidence to support generalizations. Present and defend opinions by making judgments about information, the validity of ideas or quality of work based on a set of criteria. Compile information together in a different way by combining elements in a new pattern or proposing alternative solutions.	21	30

1. No chapter wise weightage. Care to be taken to cover all the chapters.
2. Suitable internal variations may be made for generating various templates.

Choice(s):

- There will be no overall choice in the question paper.
- However, 33% internal choices will be given in all the sections.

Contents

1.	Solutions	 1
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CHAPTER

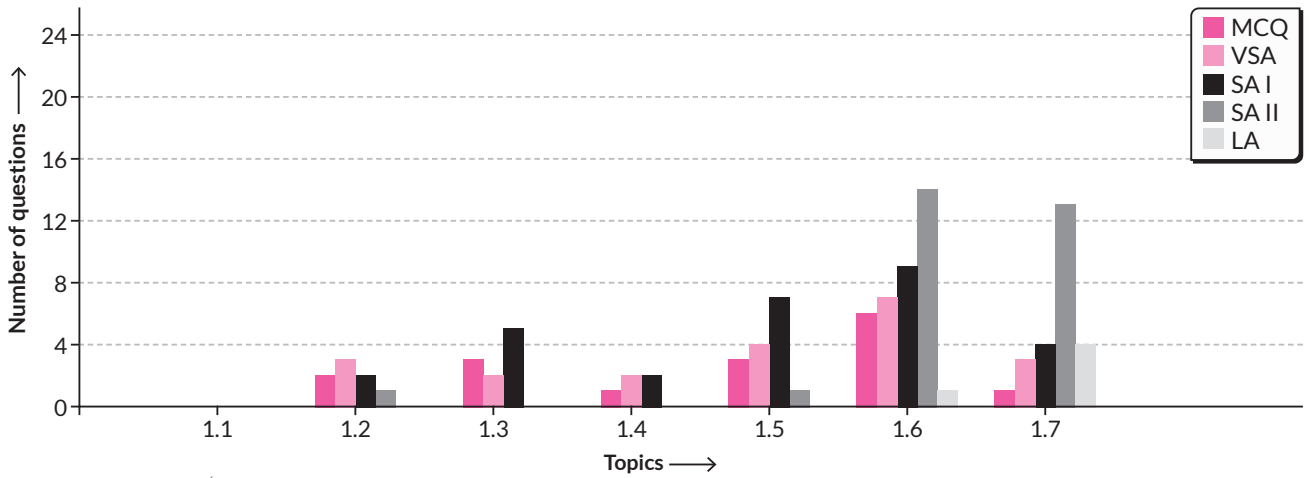
1

Solutions

TOPICS

1.1 Types of Solutions
1.2 Expressing Concentration of Solutions
1.3 Solubility
1.4 Vapour Pressure of Liquid Solutions
1.5 Ideal and Non-ideal Solutions
1.6 Colligative Properties and Determination of Molar Mass
1.7 Abnormal Molar Masses

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topics 1.5, 1.6 and 1.7 are highly scoring topics.
- Maximum total weightage is of Topic 1.6 *Colligative Properties and Determination of Molar Mass.*
- Maximum MCQ, VSA, SA I and SA II type questions were asked from Topic 1.6 *Colligative Properties and Determination of Molar Mass.*

QUICK RECAP

- **Solution :** A perfectly homogeneous mixture of two or more components is called *solution*.
- **Solute :** The component which is present in lesser amount or whose physical state is changed during the formation of solution is called *solute*.
- **Solvent :** The component which is present in larger amount and determines the physical state of the solution is called *solvent*.
- **Types of solution :** Depending upon the nature of solute and solvent, solutions are classified as follows :
  - **Gaseous solutions :** Solutions in which gas acts as solvent.

Solute	Solvent	Examples
Solid	Gas	Iodine vapours in air, dust or smoke particles in air
Liquid	Gas	Water vapours in air
Gas	Gas	Air

- **Liquid solutions :** Solutions in which liquids are present in larger amount.

Solute	Solvent	Examples
Solid	Liquid	Salt/sugar in water
Liquid	Liquid	Alcohol in water
Gas	Liquid	Aerated drinks, O_2 in water

- **Solid solutions :** Solutions in which solids are present in larger amount.

Solute	Solvent	Examples
Solid	Solid	Alloys
Liquid	Solid	Hg in Ag, Hg in Zn (Amalgam)
Gas	Solid	Solution of hydrogen in palladium.

Different methods for expressing concentration of solution :

Method of expressing	Formula
Mass percentage	$\left(\frac{w}{W}\right)\% = \frac{w_2}{(w_1+w_2)} \times 100$
Volume percentage	$\left(\frac{v}{V}\right)\% = \frac{V_2}{(V_1+V_2)} \times 100$
Mass by volume percentage	$\left(\frac{w}{V}\right)\% = \frac{w_2}{V_{solution}(\text{in mL})} \times 100$
Mass fraction	$x_1 = \frac{w_1}{w_1+w_2}$ or $x_2 = \frac{w_2}{w_1+w_2}$
Strength ($g\ L^{-1}$)	$\frac{w_2(\text{in g})}{V_{solution}(\text{in mL})} \times 1000$
Parts per million (ppm)	$\frac{w_2}{(w_1+w_2)} \times 10^6$
Molarity, (M) ($mol\ L^{-1}$)	$\frac{w_2 \times 1000}{M_2 \times V_{solution}(\text{in mL})}$
Molality, (m) ($mol\ kg^{-1}$)	$\frac{w_2 \times 1000}{M_2 \times w_1(\text{in g})}$
Mole fraction, (x_i)	$x_1 = \frac{n_1}{n_1+n_2}$ or $x_2 = \frac{n_2}{n_1+n_2}$ $(x_1 + x_2 = 1)$ In case of gases only, $y_1 = \frac{p_1}{p_1+p_2}$ or $y_2 = \frac{p_2}{p_1+p_2}$ $(y_1 + y_2 = 1)$

Solubility : Maximum amount of substance that can be dissolved in a specified amount of solvent at a specified temperature is called its *solubility*.

Factors affecting solubility of a solid in a liquid :

- **Nature of solute and solvent :** Polar solutes dissolve in polar solvents and non-polar solutes dissolve in non-polar solvents. (*i.e.*, like dissolves like).
- **Effect of temperature :**
  - If the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility **increases** with **rise** in temperature.
  - If dissolution process is exothermic ($\Delta_{sol}H < 0$), the solubility **decreases** with **rise** in temperature.
- **Effect of pressure :** Pressure does not have any significant effect on solubility of solids in liquids as these are highly incompressible.

Factors affecting solubility of a gas in a liquid :

- **Effect of pressure : Henry's law** states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution."
  $p = K_H x$ where, K_H is the Henry's law constant and is different for different gases at a particular temperature.
  Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
- **Effect of temperature :** As dissolution is an **exothermic** process, then according to Le Chatelier's principle, the solubility should **decrease** with **increase of temperature**.

Raoult's law : It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. $p_1 = x_1 p_1^\circ$ and $p_2 = x_2 p_2^\circ$; where p_1° and p_2° are vapour pressures of pure components 1 and 2 respectively, at the same temperature.

Dalton's law of partial pressures :

$P_{total} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ = (1 - x_2) p_1^\circ + x_2 p_2^\circ = p_1^\circ + (p_2^\circ - p_1^\circ) x_2$

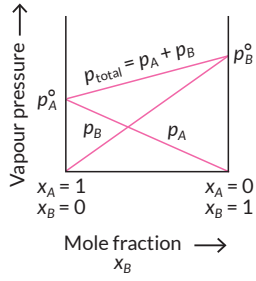
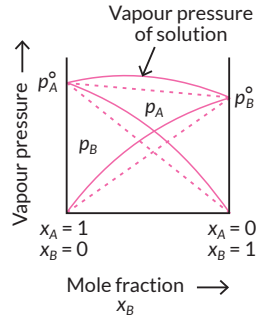
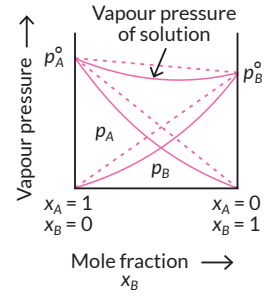
If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase then, $p_1 = y_1 P_{total}$ and $p_2 = y_2 P_{total}$

Raoult's law for solid-liquid solutions : It states that relative lowering in vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute.

$$\frac{p^\circ - p_s}{p^\circ} = x_2$$

where, p° = vapour pressure of pure solvent
p_s = vapour pressure of solution
x_2 = mole fraction of solute.

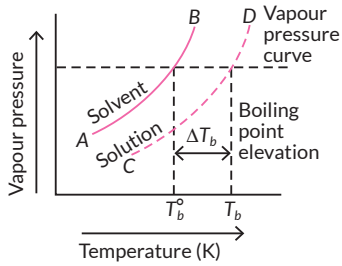
Ideal and non-ideal solutions :

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	**Negative deviation from Raoult's law**
		
$A - B$ interactions = $A - A$ and $B - B$ interactions	$A - B$ interactions << $A - A$ and $B - B$ interactions	$A - B$ interactions >> $A - A$ and $B - B$ interactions
$\Delta H_{mix} = 0, \Delta V_{mix} = 0$	$\Delta H_{mix} > 0, \Delta V_{mix} > 0$	$\Delta H_{mix} < 0, \Delta V_{mix} < 0$
e.g., dilute solutions, benzene + toluene, *n*-hexane + *n*-heptane	*e.g.*, acetone + ethanol, acetone + CS_2, water + methanol	*e.g.*, acetone + aniline, acetone + chloroform, HNO_3 + water

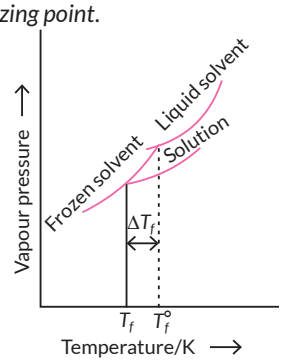
Azeotropes : The mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as vapour phase are called *constant boiling mixtures* or *azeotropic mixtures*.

- **Minimum boiling azeotropes :** They formed by those liquid pairs which show positive deviations from ideal behaviour *e.g.*, ethanol-water mixture.
- **Maximum boiling azeotropes :** They are formed by those liquid pairs which show negative deviations from ideal behaviour, *e.g.*, nitric acid-water mixture.

Colligative properties : Properties which depend only on the number of solute particles dissolved in a definite amount of the solvent and do not depend on the nature of the solute are called *colligative properties*.

Colligative properties	Expression
Relative lowering of vapour pressure : When a non- volatile solute is dissolved in a solvent, vapour pressure of the solution is lower than that of the pure solvent which is known as *lowering of vapour pressure*. Relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.	$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{w_2 \times M_1}{M_2 \times w_1}$ ($\because$ for dilute solutions, $n_2 << n_1$)
Elevation in boiling point : The boiling point of a solution containing a non-volatile solute is always higher than the boiling point of the pure solvent. This increase in boiling point is termed as *elevation in boiling point*. 	$\Delta T_b = T_b - T_b^\circ$ $\Delta T_b \propto m$ or $\Delta T_b = K_b m$ $= K_b \left(\frac{w_2 \times 1000}{M_2 \times w_1 (\text{in g})} \right)$ or $M_2 = \frac{K_b \times w_2 \times 1000}{\Delta T_b \times w_1 (\text{in g})}$ K_b is called boiling point elevation constant or molal elevation constant or ebullioscopic constant, having unit K kg mol^{-1}.

Depression in freezing point : The freezing point of a solution containing a non-volatile solute is always less than the freezing point of the pure solvent. This decrease in freezing point is termed as *depression in freezing point*.



$\Delta T_f = T_f^\circ - T_f$

$\Delta T_f \propto m$ or $\Delta T_f = K_f m$

$$= K_f \left(\frac{w_2 \times 1000}{M_2 \times w_1 (\text{in g})} \right)$$

or $M_2 = \dfrac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1 (\text{in g})}$

K_f is known as freezing point depression constant or molal depression constant or cryoscopic constant, having unit K kg mol^{-1}.

Osmotic pressure : The movement of solvent molecules from less concentrated solution to more concentrated solution through semipermeable membrane is termed as *osmosis*. The hydrostatic pressure which develops on account of osmosis is called *osmotic pressure* or the excess pressure that must be applied on the solution to prevent osmosis is called *osmotic pressure*.

$\pi = CRT = \left(\dfrac{n_2}{V} \right) RT$,

$\pi V = \dfrac{w_2 RT}{M_2}$ or $M_2 = \dfrac{w_2 RT}{\pi V}$

- Two solutions having same osmotic pressure at a given temperature are called *isotonic solutions*.
- If one solution is of lower osmotic pressure, it is called *hypotonic* with respect to the more concentrated solution. The more concentrated solution is said to be *hypertonic* with respect to the dilute solution.
- If a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semipermeable membrane and the process is called *reverse osmosis*. It is used in *desalination of sea water*.

Abnormal molecular mass : When the molecular mass of a substance determined by any of the colligative properties comes out to be different than the expected value, the substance is said to show *abnormal molecular mass*.

- Abnormal molecular masses are observed when the solution is non-ideal (not dilute) or the solute undergoes *association* or *dissociation*.

van't Hoff Factor : It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$$

$$i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Total number of moles of particles before association/dissociation}}$$

- If $i > 1$, solute undergoes dissociation in the solution and if $i < 1$, solute undergoes association in the solution.

$$\alpha_{\text{dissociation}} = \frac{i-1}{n-1} ;$$

$$\alpha_{\text{association}} = \frac{1-i}{1-\frac{1}{n}}$$

- For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows :

$$\frac{p_1^\circ - p_1}{p_1^\circ} = ix_2 ; \Delta T_b = iK_b m; \ \Delta T_f = iK_f m; \ \pi = iCRT$$

BRAIN MAP

SOLUTIONS

A solution is a homogeneous mixture of two or more substances whose composition can be varied with certain limits. The component of solution present in larger quantity is called solvent while the component present in lesser quantity is called solute.

Composition of Solutions : Expressing Concentration of Solution

Mass percentage :

$$\text{Mass \% of the solution} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

Parts per million : ppm of A = $\frac{\text{Mass of component } A}{\text{Total mass of solution}} \times 10^6$

Molarity :

$$\text{Molarity } (M) = \frac{\text{Moles of solute}}{\text{Volume of solution (mL)}} \times 1000$$

Molality :

$$\text{Molality } (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent in grams}} \times 1000$$

Mole Fraction :

$$\text{Mole fraction of a component} = \frac{\text{No. of moles of the component}}{\text{Total no. of moles of all component}}$$

Normality :

$$\text{Normality } (N) = \frac{\text{No. of gram equivalent of solute}}{\text{Volume of solution in mL}} \times 1000$$

Formality :

$$\text{Formality } (F) = \frac{\text{No. of formula masses of solute}}{\text{Volume of solution in litre}}$$

Abnormal molar mass and van't Hoff factor :

$$i = \frac{\text{Observed value of colligative property}}{\text{Normal value of colligative property}} = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$$

For solute undergoing association : $\alpha = (1 - i)\frac{n}{n-1}; i < 1$

For solute undergoing dissociation : $\alpha = \frac{i-1}{n-1}; i > 1$

Modified colligative properties :

$$\frac{p^\circ - p_s}{p^\circ} = ix_2 \; ; \Delta T_b = iK_b m, \Delta T_f = iK_f m; \pi = iCRT$$

Laws

Henry's Law : The law states that "the mass of a gas (m) dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure (p) the gas in equilibrium with the solution."

$m \propto p$; $m = K_H p$

$x_A = K_H p$

where,

K_H = Henry's constant

Raoult's Law : The law states that "at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component in solution is equal to the product of the vapour pressure of pure component and its mole fraction".

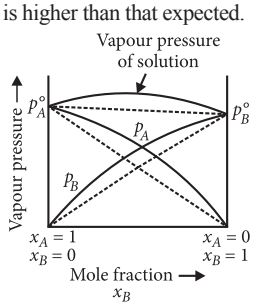
$P_A = p_A^\circ \times x_A$; $P_B = p_B^\circ \times x_B$

Types of Solution

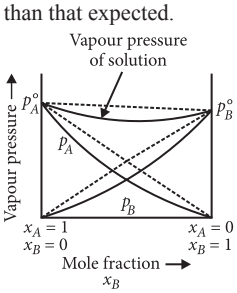
Ideal solutions : $A - B$ interactions are of same magnitude as $A - A$ and $B - B$ interactions, $\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$.

Non-ideal solutions : $A - B$ interactions are of different magnitude than $A - A$ and $B - B$ interactions, $\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$.

– **Non-ideal solutions showing +ve deviations :** $A - B$ interactions are weaker than $A - A$ and $B - B$ interactions, ΔV_{mix} = +ve, ΔH_{mix} = +ve and resulting vapour pressure is higher than that expected.



– **Non-ideal solutions showing –ve deviations :** A–B interactions are stronger than $A - A$ and $B - B$ interactions, ΔV_{mix} = –ve, ΔH_{mix} = –ve and resulting vapour pressure is lower than that expected.



Azeotropes : Constant boiling mixtures.

Colligative Properties

Relative lowering in vapour pressure : The relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute (X_B) at a given temperature.

$$\frac{p_A^\circ - p_A}{p_A^\circ} = X_B$$

Elevation in boiling point : Elevation in boiling point (*i.e.*, ΔT_b) is directly proportional to the molality (m) of the solute in solution.

$\Delta T_b \propto m$

$\Delta T_b = K_b m$

where,

K_b = molal boiling point elevation constant.

Depression in freezing point : Depression in freezing point (*i.e.*, ΔT_f) is directly proportional to the molal concentration of solute (m).

$\Delta T_f \propto m$

$\Delta T_f = K_f m$

where,

K_f = molal freezing point depression constant.

Osmotic Pressure : At any temperature, the osmotic pressure (π) of a solution is proportional to the molar concentration (C) of the solute and absolute temperature.

$\pi = CRT$

where, R = universal gas constant.

Previous Years' CBSE Board Questions

1.2 Expressing Concentration of Solutions

Mass Percentage, Mole Fraction, Molarity, Molality

MCQ

1. **Assertion (A) :** Molality of a solution in liquid state changes with temperature.
Reason (R) : The volume of solution changes with the change in temperature.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020 C)*

2. 50 mL of an aqueous solution of glucose $C_6H_{12}O_6$ (Molar mass : 180 g/mol) contains 6.02×10^{22} molecules. The concentration of the solution will be
(a) 0.1 M (b) 0.2 M
(c) 1.0 M (d) 2.0 M *(2020)*

VSA (1 mark)

3. Define the following term : Molality (*m*)
(NCERT, 1/2, Delhi 2017, 1/5 AI 2014 C) R

4. Define the following term : Molarity (*M*)
(NCERT, 1/2, Delhi 2017, 1/5 AI 2014) R

5. Define the following term :
Mole fraction *(NCERT, 1/5 AI 2014 C)* R

SA I (2 marks)

6. Calculate the molarity of 9.8% (*w*/*W*) solution of H_2SO_4 if the density of the solution is 1.02 g mL^{-1}. (Molar mass of H_2SO_4 = 98 g mol^{-1})
(2/5, Foreign 2014) Ev

7. Differentiate between molarity and molality of a solution. How can we change molality value of a solution into molarity value? *(Delhi 2014 C)* An

SA II (3 marks)

8. A solution of glucose (molar mass = 180 g mol^{-1}) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution?
(Density of solution = 1.2 g mL^{-1})
(NCERT, 3/5, AI 2014)

1.3 Solubility

Solubility of Gas in a Liquid (Henry's Law)

MCQ

9. On dissolving ammonium chloride in water at room temperature, the solution feels cool to touch. Under which of the following conditions does salt dissolve faster?
(a) Powdered salt in cold water
(b) Powdered salt in hot water
(c) Salt crystals in cold water
(d) Salt crystals in hot water *(2023)*

10. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to
(a) high atmospheric pressure
(b) low temperature
(c) low atmospheric pressure
(d) both low temperature and high atmospheric pressure. *(2023)*

11. An unknown gas '*X*' is dissolved in water at 2.5 bar pressure and has mole fraction 0.04 in solution. The mole fraction of '*X*' gas when the pressure of gas is doubled at the same temperature is
(a) 0.08 (b) 0.04 (c) 0.02 (d) 0.92
(Term I, 2021-22) An

VSA (1 mark)

12. Why aquatic animals are more comfortable in cold water than in warm water? *(1/3, 2018)* Ap

13. Gas (*A*) is more soluble in water than gas (*B*) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why?
(1/2, AI 2016)

SA I (2 marks)

14. What is Henry's law? Give one application of it. *(2023)*

15. State Henry's law. Why is air diluted with helium in the tanks used by scuba divers? *(2/5, 2020)* An

16. State Henry's law. Calculate the solubility of CO_2 in water at 298 K under 760 mm Hg.
(K_H for CO_2 in water at 298 K is 1.25×10^6 mm Hg)
(2020)

17. State Henry's law and mention two of its important applications. *(2020 C)* U

18. Give reasons for the following.
(a) Aquatic species are more comfortable in cold water than in warm water.
(b) At higher altitudes people suffer from anoxia resulting in inability to think. *(AI 2019)* Ap

1.4 Vapour Pressure of Liquid Solutions

Raoult's Law

MCQ

19. Which of the following formula represents Raoult's law for a solution containing non-volatile solute?
(a) $p_{solute} = p^{\circ}_{solute} \cdot x_{solute}$
(b) $p = K_H \cdot x$
(c) $P_{total} = p_{solvent}$
(d) $p_{solute} = p^{\circ}_{solvent} \cdot x_{solvent}$
(Term I, 2021-22) U

VSA (1 mark)

20. Identify which liquid will have a higher vapour pressure at 90°C if the boiling points of two liquids *A* and *B* are 140°C and 180°C, respectively.
(One word, 2020) U

21. Define Raoult's law. *(1/5 AI 2014C)*

SA I (2 marks)

22. State Raoult's law for a solution containing volatile components. What is the similarity between Raoult's law and Henry's law? *(2020, Delhi 2014)* R

23. State Raoult's law for a solution containing volatile components. Name the solution which follows Raoult's law at all concentrations and temperatures.
(2/5, Foreign 2014) R

1.5 Ideal and Non-ideal Solutions

Ideal Solutions

MCQ

24. Which one of the following pairs will form an ideal solution?
(a) Chloroform and acetone
(b) Ethanol and acetone
(c) *n*-Hexane and *n*-heptane
(d) Phenol and aniline *(Term I, 2021-22)* Ap

VSA (1 mark)

25. Define the following term : Ideal solution
(1/2, Delhi 2017, 1/5, AI 2017 C)

SA II (3 marks)

26. (a) Differentiate between Ideal solution and Non-ideal solution.
(b) 30 g of urea is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg. *(2023)*

Non-ideal Solutions

MCQ

27. On mixing 20 mL of acetone with 30 mL of chloroform, the total volume of the solution is
(a) < 50 mL (b) = 50 mL
(c) > 50 mL (d) = 10 mL
(Term I, 2021-22) Ev

VSA (1 mark)

28. What happens when acetone is added to pure ethanol? *(1/2, 2020)* Ev

SA I (2 marks)

29. What type of deviation from Raoult's law is observed by mixing chloroform and acetone?
Why is a decrease in a vapour pressure observed in mixing chloroform and acetone? *(2021C)* Ap

30. Write two differences between ideal solutions and non-ideal solutions.
(2/3, 2020 C, Delhi 2019, 2/5, AI 2017)

31. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation? *(Delhi 2015)*

OR

What is meant by negative deviation from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for negative deviation? *(Foreign 2015)*

32. What type of deviation is shown by a mixture of ethanol and acetone? Give reason. *(2/5, AI 2014)*

Azeotropes

MCQ

33. An azeotropic solution of two liquids has a boiling point lower than either of the two when it
(a) shows a positive deviation from Raoult's law
(b) shows a negative deviation from Raoult's law
(c) shows no deviation from Raoult's law
(d) is saturated. *(Term I, 2021-22)*

VSA (1 mark)

34. In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes?
(1/2, AI 2016)

35. Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? *(Delhi 2014)*

OR

Define the following term :
Azeotrope *(1/5, Foreign 2014)*

SA I (2 marks)

36. What type of azeotropic mixture will be formed by a solution of acetone and chloroform? Justify on the basis of strength of intermolecular interactions that develop in the solution. *(AI 2019)* U

37. Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. *(Delhi 2015)*

38. Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. *(Foreign 2015)*

1.6 Colligative Properties and Determination of Molar Mass

Relative Lowering in Vapour Pressure

VSA (1 mark)

39. Define the following term :
Colligative properties *(1/2, Delhi 2017)*

40. How is the vapour pressure of a solvent affected when a non-volatile solute is dissolved in it?
(1/2, Delhi 2014C) U

SA I (2 marks)

41. A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 308 K. Calculate the molar mass of the solute.
(Vapour pressure of pure water at 308 K = 32 mm Hg) *(2023)*

SA II (3 marks)

42. Give reasons :
(a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.
(b) Aquatic animals are more comfortable in cold water than in warm water.
(c) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution. *(2023)*

43. Vapour pressure of water at 293 K is 17·536 mm Hg. Calculate the vapour pressure of aqueous solution when 20 g of glucose (Molar mass = 180 g mol^{-1}) is dissolved in 500 g of water. *(2021 C)*

44. 30 g of urea (M = 60 g mol^{-1}) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg. *(3/5, AI 2017)*

LA (5 marks)

45. (a) State Henry's law and mention its two applications.
(b) 5% aqueous solution of a non-volatile solute was made and its vapour pressure at 373 K was found to be 745 mm. Vapour pressure of pure water at this temperature was 760 mm. Calculate the molar mass of solute.
(2020C) Ap

Elevation of Boiling Point

MCQ

46. The boiling point of a 0.2 m solution of a non-electrolyte in water is
(K_b for water = 0.52 K kg mol^{-1})
(a) 100 °C (b) 100.52 °C
(c) 100.104 °C (d) 100.26 °C
(Term I, 2021-22) Cr

47. **Assertion (A) :** Elevation in boiling point is a colligative property.
Reason (R) : Elevation in boiling point is directly proportional to molarity.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is wrong statement.
(d) Assertion (A) is wrong, but Reason (R) is correct statement. *(2020)* R

VSA (1 mark)

48. Define the following term :
Molal elevation constant (K_b) *(1/5, AI 2014)*

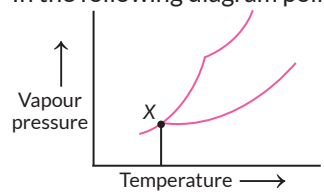
SA I (2 marks)

49. Why does a solution containing non-volatile solute have higher boiling point than the pure solvent? Why is elevation of boiling point a colligative property?
(AI 2015) An

Depression of Freezing Point

MCQ

50. In the following diagram point '*X*' represents



(a) boiling point of solution
(b) freezing point of solvent
(c) boiling point of solvent
(d) freezing point of solution.
(Term I, 2021-22) Cr

SA I (2 marks)

51. Nisha took two aqueous solutions – one containing 7.5 g of urea (Molar mass = 60 g/mol) and the other containing 42.75 g of substance *Z* in 100 g of water, respectively. It was observed that both the solutions froze at the same temperature. Calculate the molar mass of *Z*. *(2020)* Ev

52. Calculate the freezing point of a solution containing 60 g of glucose (molar mass = 180 g mol^{-1}) in 250 g of water. (K_f of water = 1.86 K kg mol^{-1}) *(2018)*

53. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K. (K_f = 5.12 K kg mol^{-1}). *(Delhi 2014)*

SA II (3 marks)

54. An antifreeze solution is prepared by dissolving 31 g of ethylene glycol (Molar mass = 62 g mol^{-1}) in 600 g of water. Calculate the freezing point of the solution. (K_f for water = 1.86 K kg mol^{-1}) *(2020)*

55. Calculate the mass of ascorbic acid (Molar mass = 176 g mol^{-1}) to be dissolved in 75 g of acetic acid, to lower its freezing point by 1.5°C . (K_f = 3.9 K kg mol^{-1}) *(NCERT Intext, 2020)*

56. A 4% solution (*w*/*w*) of sucrose (M = 342 g mol^{-1}) in water has a freezing point of 271.15 K. Calculate the freezing point of 5% glucose (M = 180 g mol^{-1}) in water. (Given : Freezing point of pure water = 273.15 K) *(Delhi 2019)* Ev

57. 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute. *(3/5, Delhi 2019 C)*

58. A 5% solution (by mass) of cane-sugar in water has freezing point of 271 K. Calculate the freezing point of 5% solution (by mass) of glucose in water if the freezing point of pure water is 273.15 K.
[Molecular masses : Glucose $C_6H_{12}O_6$: 180 amu; Cane-sugar $C_{12}H_{22}O_{11}$: 342 amu]
(NCERT, 3/5, Delhi 2019C) Ev

59. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.
(Given : Molar mass of sucrose = 342 g mol^{-1}, molar mass of glucose = 180 g mol^{-1}) *(Delhi 2017)* Ev

60. Calculate the freezing point of the solution when 31 g of ethylene glycol ($C_2H_6O_2$) is dissolved in 500 g of water. (K_f for water = 1.86 K kg mol^{-1}) *(AI 2015)*

61. Some ethylene glycol, $HOCH_2CH_2OH$, is added to your car's cooling system along with 5 kg of water. If the freezing point of water-glycol solution is –15.0°C, what is the boiling point of the solution?
(K_b = 0.52 K kg mol^{-1} and K_f = 1.86 K kg mol^{-1} for water) *(Delhi 2014 C)*

Osmosis and Osmotic Pressure

MCQ

62. The colligative property used for the determination of molar mass of polymers and proteins is
(a) osmotic pressure
(b) depression in freezing point
(c) relative lowering in vapour pressure
(d) elevation in boiling point. *(2023)*

63. **Assertion(A) :** A raw mango placed in saline solution loses water and shrivel into pickle.
Reason (R) : Through the process of reverse osmosis raw mango shrivel into pickle.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(Term I, 2021-22)* Ap

64. **Assertion (A) :** Osmotic pressure is a colligative property.
Reason (R) : Osmotic pressure is directly proportional to molarity.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

VSA (1 mark)

65. What happens when a pressure greater than osmotic pressure is applied on the solution side separated from solvent by a semi-permeable membrane? *(1/2, 2020)* Ap

66. Give reason for the following :
Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers. *(1/2, 2018)* U

67. Define the following term :
Osmotic pressure *(1/5, AI 2017 C)* R

68. What are isotonic solutions? *(Delhi 2014)* R

SA I (2 marks)

69. For a 5% solution of urea (Molar mass = 60 g/mol), calculate the osmotic pressure at 300 K. [R = 0.0821 L atm K^{-1} mol^{-1}] *(2020)*

70. Give reasons :
(a) Cooking is faster in pressure cooker than in cooking pan.
(b) Red Blood Cells (RBC) shrink when placed in saline water but swell in distilled water. *(2019)*

71. (i) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?

(ii) What happens when the external pressure applied becomes more than the osmotic pressure of solution? *(2/5, Delhi 2016)* An

72. Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing
(i) 1.2% sodium chloride solution?
(ii) 0.4% sodium chloride solution?
(2/5, Delhi 2016) Ap

SA II (3 marks)

73. At 300 K, 30 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of a glucose solution is 1.52 bar at the same temperature, what would be its concentration? *(AI 2019)*

74. A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. *(3/5, AI 2014)*

75. Define the following terms :
(i) Osmotic pressure
(ii) Colligative properties *(Foreign 2014)* R

1.7 Abnormal Molar Masses

van't Hoff and Abnormal Molar Mass

VSA (1 mark)

76. Define the following term :
van't Hoff factor *(Delhi 2017)*

77. Define the following term :
Abnormal molar mass *(Delhi 2017)*

SA I (2 marks)

78. Predict the state of the solute in the solution in the following situations :
(a) When '*i*' is found to be more than one.
(b) When '*i*' is found to be less than one. *(2020)*

79. What is van't Hoff factor? What types of values can it have if in forming the solution the solute molecules undergo
(i) dissociation
(ii) association? *(2/5, AI 2014 C)* U

van't Hoff and Elevation in Boiling Point

VSA (1 mark)

80. Give reason for the following :
Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution.
(1/2, 2018) U

SA I (2 marks)

81. Give reasons :
(i) 0.1 M KCl has higher boiling point than 0.1 M glucose.
(ii) Meat is preserved for a longer time by salting.
(2020) An

SA II (3 mark)

82. (a) Out of 0·1 molal aqueous solution of glucose and 0·1 molal aqueous solution of KCl, which one will have higher boiling point and why ?
(b) Predict whether van't Hoff factor, (*i*) is less than one or greater than one in the following :
(i) CH_3COOH dissolved in water
(ii) CH_3COOH dissolved in benzene *(2019)*

83. Calculate the boiling point elevation for a solution prepared by adding 10 g of $CaCl_2$ to 200 g of water. (K_b for water = 0.52 K kg mol^{-1}, molar mass of $CaCl_2$ = 111 g mol^{-1}) *(3/5, AI 2017C, Foreign 2014)*

84. Calculate the boiling point of solution when 4 g of $MgSO_4$ (M = 120 g mol^{-1}) was dissolved in 100 g of water, assuming $MgSO_4$ undergoes complete ionization.
(K_b for water = 0.52 K kg mol^{-1}) *(AI 2016)*

LA (5 marks)

85. (i) Why is boiling point of 1 M NaCl solution more than that of 1 M glucose solution?
(ii) A non-volatile solute *X* (molar mass = 50 g mol^{-1}) when dissolved in 78 g of benzene reduced its vapour pressure to 90%. Calculate the mass of *X* dissolved in the solution.
(iii) Calculate the boiling point of elevation for a solution prepared by adding 10g of $MgCl_2$ to 200 g of water assuming $MgCl_2$ is completely dissociated.
(K_b for water = 0.512 K kg mol^{-1}, molar mass $MgCl_2$ = 95 g mol^{-1}) *(2023)*

van't Hoff and Depression in Freezing Point

MCQ

86. Out of the following 1.0 M aqueous solutions which one will show largest freezing point depression?
(a) NaCl (b) Na_2SO_4
(c) $C_6H_{12}O_6$ (d) $Al_2(SO_4)_3$ *(2023)*

SA I (2 marks)

87. Assuming complete dissociation, calculate the expected freezing point of a solution prepared by dissolving 6.00 g of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$ in 0.100 kg of water. (K_f for water = 1.86 K kg mol^{-1}, atomic masses : Na = 23, S = 32, O = 16, H = 1)
(2/5, AI 2014C) Ap

SA II (3 marks)

88. When 19.5 g of $F—CH_2—COOH$ (molar mass = 78 g mol^{-1}) is dissolved in 500 g of water, the depression

in freezing point is observed to be 1°C. Calculate the degree of dissociation of F—CH_2—COOH.
[Given : K_f for water = 1.86 K kg mol^{-1}] *(3/5, 2020)* Ev

89. The freezing point of a solution containing 5 g of benzoic acid (M = 122 g mol^{-1}) in 35 g of benzene is depressed by 2.94 K. What is the percentage association of benzoic acid if it forms a dimer in solution? (K_f for benzene = 4.9 K kg mol^{-1}) *(2020)* An

90. A 0.01 m aqueous solution of $AlCl_3$ freezes at –0.068 °C. Calculate the percentage of dissociation.
[Given : K_f for water = 1.86 K kg mol^{-1}] *(2020)* Ev

91. Calculate the freezing point of solution when 1.9 g of $MgCl_2$ (M = 95 g mol^{-1}) was dissolved in 50 g of water, assuming $MgCl_2$ undergoes complete ionization.
(K_f for water = 1.86 K kg mol^{-1}) *(Delhi 2016)*

92. When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x). (K_f for CS_2 = 3.83 K kg mol^{-1}, atomic mass of sulphur = 32 g mol^{-1})
(3/5 Delhi 2016) Cr

93. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).
(Given : Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1}) *(Delhi 2015)* Ev

94. Calculate the mass of NaCl (molar mass = 58.5 g mol^{-1}) to be dissolved in 37.2 g of water to lower the freezing point by 2°C, assuming that NaCl undergoes complete dissociation. (K_f for water = 1.86 K kg mol^{-1})
(Foreign 2015)

LA (5 marks)

95. (a) Give two differences between ideal and non-ideal solutions.
(b) Calculate the amount of NaCl (M = 58.5 g mol^{-1}) that must be added to 100 g of water so that freezing point is depressed by 2 K. K_f for water is 1.86 K/m. *(2020C)*

96. (a) Write two characteristics of non-ideal solution.
(b) 2 g of benzoic (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution ?
(2019)

van't Hoff and Osmotic Pressure

SA II (3 marks)

97. A solution contains 5.85 g NaCl (Molar mass = 58.5 g mol^{-1}) per litre of solution. It has an osmotic pressure of 4.75 atm at 27°C. Calculate the degree of dissociation of NaCl in this solution.
(Given : R = 0.082 L atm K^{-1} mol^{-1}) *(3/5, 2020)*

98. A solution 0.1 M of Na_2SO_4 is dissolved to the extent of 95%. What would be its osmotic pressure at 27°C?
(R = 0.0821 L atm K^{-1} mol^{-1}) *(2019)*

99. (a) Draw the graph between vapour pressure and temperature and explain the elevation in boiling point of a solvent in solution.
(b) Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litres of water at 25°C assuming it to be completely dissociated.
(Atomic masses : K = 39 u, S = 32 u, O = 16 u)
(2019)

LA (5 marks)

100. (i) What is the value of van't Hoff factor for ethanoic acid in benzene close to 0.5?
(ii) Determine the osmotic pressure of a solution prepared by dissolving 2.32 × 10^{-2} g of K_2SO_4 in 2 L of solution at 25°C, assuming that K_2SO_4 is completely dissociated.
(iii) When 25.6 g of sulphur was dissolved in 1000 g of benzene, the freezing point lowered by 0.512 K. Calculate the formula of sulphur (S_x).
(K_f for benzene = 5.12 K kg mol^{-1}, Atomic mass of sulphur = 32 g mol^{-1}) *(2023)*

CBSE Sample Questions

1.2 Expressing Concentration of Solutions

MCQ

1. Given below are two statements labelled as assertion (A) and Reason (R).
Assertion (A) : Molarity of a solution changes with temperature.
Reason (R) : Molarity is a colligative property.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(Term I, 2021-22)* R

1.3 Solubility

MCQ

2. Solubility of gases in liquids decreases with rise in temperature because dissolution is an

(a) endothermic and reversible process
(b) exothermic and reversible process
(c) endothermic and irreversible process
(d) exothermic and irreversible process.

(*Term I, 2021-22*)

In the following question a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

3. **Assertion :** Aquatic species are more comfortable in cold waters rather than in warm waters.
Reason : Different gases have different K_H values at the same temperature. (*2020-21*)

SA II (3 marks)

4. Answer the following questions :
(a) State Henry's law and explain why are the tanks used by scuba divers filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen)?
(b) Assume that argon exerts a partial pressure of 6 bar. Calculate the solubility of argon gas in water. (Given Henry's law constant for argon dissolved in water, K_H = 40 kbar) (*2022-23*)

1.4 Vapour Pressure of Liquid Solutions

MCQ

5. Identify the law which is stated as
"For any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction."
(a) Henry's law (b) Raoult's law
(c) Dalton's law (d) Gay-Lussac's Law

(*Term I, 2021-22*) Ap

6. When 1 mole of benzene is mixed with 1 mole of toluene the vapour will contain
(Given : Vapour pressure of benzene = 12.8 kPa and vapour pressure of toluene = 3.85 kPa).
(a) equal amount of benzene and toluene as it forms an ideal solution
(b) unequal amount of benzene and toluene as it forms a non-ideal solution
(c) higher percentage of benzene
(d) higher percentage of toluene. (*2020-21*) U

1.5 Ideal and Non-ideal Solutions

MCQ

In the following question a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

7. **Assertion :** Nitric acid and water form maximum boiling azeotrope.
Reason : Azeotropes are binary mixtures having the same composition in liquid and vapour phase.

(*2020-21*)

1.6 Colligative Properties and Determination of Molar Mass

MCQ

8. In which of the following cases blood cells will shrink?
(a) When placed in water containing more than 0.9% (mass/ volume) NaCl solution.
(b) When placed in water containing less than 0.9% (mass /volume) NaCl solution.
(c) When placed in water containing 0.9% (mass/ volume) NaCl solution.
(d) When placed in distilled water.

(*Term I, 2021-22*) An

9. How much ethyl alcohol must be added to 1 litre of water so that the solution will freeze at – 14°C ? (K_f for water = 1.86°C/mol)
(a) 7.5 mol (b) 8.5 mol
(c) 9.5 mol (d) 10.5 mol

(*Term I, 2021-22*)

10. Water retention or puffiness due to high salt intake occurs due to
(a) diffusion
(b) vapour pressure difference
(c) osmosis
(d) reverse osmosis. (*Term I, 2021-22*)

11. Given below are two statements labelled as assertion (A) and Reason (R).
Assertion (A) : Cryoscopic constant depends on nature of solvent.
Reason (R) : Cryoscopic constant is a universal constant.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.
(d) A is false but R is true. (2020-21) U

SA I (2 marks)

12. A glucose solution boils at 101.04°C at 1 atm. What will be relative lowering of vapour pressure of an aqueous solution of urea which is equimolal to given glucose solution?
(Given : K_b for water is 0.52 K kg mol^{-1}) (2020-21) Ev

1.7 Abnormal Molar Masses

Case Based (4 marks)

13. Henna is investigating the melting point of different salt solutions.
She makes a salt solution using 10 mL of water with a known mass of NaCl salt.
She puts the salt solution into a freezer and leaves it to freeze. She takes the frozen salt solution out of the freezer and measures the temperature when the frozen salt solution melts. She repeats each experiment.

S.No.	Mass of the salt used in g	Melting point in °C	
		Readings Set 1	Readings Set 2
1	0.3	−1.9	−1.9
2	0.4	−2.5	−2.6
3	0.5	−3.0	−5.5
4	0.6	−3.8	−3.8
5	0.8	−5.1	−5.0
6	1.0	−6.4	−6.3

Assuming the melting point of pure water as 0°C, answer the following questions :
(a) One temperature in the second set of results does not fit the pattern. Which temperature is that? Justify your answer.
(b) Why did Henna collect two sets of results?
(c) In place of NaCl, if Henna had used glucose, what would have been the melting point of the solution with 0.6 g glucose in it?

OR

What is predicted melting point, if 1.2 g of salt is added to 10 mL of water? Justify your answer.
(2022-23)

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. (d): Molality of a solution in liquid state does not change with temperature as mass does not change with temperature. The volume of solution changes with change in temperature so, does the molarity changes.

2. (d): 1 mole of glucose = N_A molecules

6.02×10^{22} molecules $= \frac{1}{N_A} \times 6.02 \times 10^{22}$ mole = 0.1 mole

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (mL)}} \times 1000$$

$$= \frac{0.1}{50} \times 1000 = 2 \text{ mol L}^{-1} \text{ or } 2 \text{ M}$$

3. Molality (m) is defined as the number of moles of the solute per kilogram of the solvent and is expressed as :

$$\text{Molality } (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

4. It is the number of moles of the solute dissolved per litre of the solution. It is denoted by M.

$$\therefore \quad \text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{n_2}{V(\text{in mL})} \times 1000 = \frac{w_2 \times 1000}{M_2 \times V(\text{in mL})} \qquad \left(\therefore n_2 = \frac{w_2}{M_2}\right)$$

5. Mole fraction is the ratio of number of moles of solute or solvent to total number of moles of solution. It is denoted by x.

$$x_{\text{solute}} = \frac{n_2}{n_1 + n_2}, \; x_{\text{solvent}} = \frac{n_1}{n_1 + n_2}$$

6. Mass of solute = 9.8 g; Mass of solution = 100 g
Density of solution = 1.02 g mL^{-1}

$$\therefore \quad \text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$= \frac{100 \text{ g}}{1.02 \text{ g mL}^{-1}} = 98.039 \text{ mL} = 0.098 \text{ L}$$

Number of moles of solute, $n = \frac{9.8}{98} = 0.1 \text{ mol}$

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}} = \frac{0.1 \text{ mol}}{0.098 \text{ L}} = 1.02 \text{ M}$$

Answer Tips
➲ Remember unit conversion (mL into L), 1 L = 1000 mL

7.

Molarity	Molality
Number of moles of solute dissolved in one litre solution is called molarity.	Number of moles of solute dissolved in one kg solvent is called molality.
$M = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}}$	$m = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$
Molarity depends on temperature as volume depends on temperature. Molarity decreases with rise in temperature.	Molality is independent of temperature as mass does not change with temperature.

If M_B is the molar mass of solute, d is the density of solution then molality (m) of a solution can be converted to molarity (M) by using the formula, $M = \frac{md}{\left(1+\frac{mM_B}{1000}\right)}$

Commonly Made Mistake

➲ Molarity (mol L^{-1}), Molality (mol kg^{-1})

8. Given : Mass of solute, W_2 = 10 g
Mass of solvent, W_1 = 90 g
Molar mass of solute, M_2 = 180 g mol^{-1}
Density of solution = 1.2 g mL^{-1}

$$\text{Molality} = \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{10 \times 1000}{180 \times 90} = 0.62 \text{ m}$$

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.2 \text{ g mL}^{-1}}$$

$$\text{Molarity} = \frac{W_2 \times 1000}{M_2 \times V}$$

$$M = \frac{10 \times 1000}{180 \times \frac{100}{1.2}} = \frac{10 \times 1000 \times 1.2}{180 \times 100} = 0.67 \text{ M}$$

9. **(b):** Powdered salt dissolves faster in hot water. Dissolution of ammonium chloride in water is an endothermic reaction, hence high temperature will favor the dissolution of ammonium chloride in water.

10. **(c):** At high altitudes, the partial pressure of oxygen is less than at the ground level. As a result, there is a low concentration of oxygen in the blood and tissues of the people living at high altitudes.

11. **(a):** According to Henry's law, $p = K_H x$
2.5 bar = $K_H \times 0.04$

$$K_H = \frac{2.5}{0.04} = 62.5 \text{ bar}$$

When pressure is doubled, then x is
5 bar = $62.5 \times x \Rightarrow x = 0.08$

12. Increase in temperature decreases the solubility of oxygen in water. As a result, amount of dissolved oxygen decreases. It becomes more difficult to breathe as oxygen is less. Hence, the aquatic species are not comfortable in warm water.

13. According to Henry's law, the solubility of a gas is inversely proportional to the Henry's law constant (K_H) for that gas. Hence, gas (B) being less soluble, would have a higher K_H value.

14. Henry's law states that the solubility of a gas in a liquid at constant temperature is directly proportional to the pressure of the gas present above the surface of liquid or solution.

$p \propto x$ or $p = K_H x$

Here, p = partial pressure of the gas in vapour phase
x = mole fraction of the gas in the solution
K_H = Henry's law constant

Application of Henry's law :
Soft drinks and soda water bottle are sealed under high pressure to increase the solubility of CO_2.

15. Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.
$p = K_H \cdot x$ where, K_H = Henry's law constant. Different gases have different K_H values at the same temperature.
To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

16. Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.
$p = K_H \cdot x$ where, K_H = Henry's law constant. Different gases have different K_H values at the same temperature.

$$\text{Solubility of } CO_2 = \frac{p}{K_H} = \frac{760}{1.25 \times 10^6} = 6.08 \times 10^{-4}$$

17. Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.
$p = K_H \cdot x$ where, K_H = Henry's law constant. Different gases have different K_H values at the same temperature.
Applications of Henry's law :
(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
(ii) To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

18. (a) Increase in temperature decreases the solubility of oxygen in water. As a result, amount of dissolved oxygen decreases. It becomes more difficult to breathe as oxygen is less. Hence, the aquatic species are not comfortable in warm water.
(b) At high altitudes, the partial pressure of oxygen is less than at the ground level. As a result, there is a low concentration of oxygen in the blood and tissues of the people living at high altitudes. Thus, they feel weak and are unable to think properly.

Concept Applied

➲ Apply concept of solubility of gases in liquid.

19. **(c):** When a non-volatile solute added to the volatile liquid, then partial pressure is only due to volatile component.
So, $p_{total} = p_{solvent}$

20. The liquid with a lower boiling point will vaporise first and has a higher vapour pressure. Hence, liquid A will have a higher vapour pressure.

21. **Raoult's law :** For a solution of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction. Thus, for any component, partial vapour pressure, $p \propto x \Rightarrow p = p^\circ . x$
where, p° = vapour pressure of pure component
x = mole fraction of that component

22. Henry's law : It states that partial pressure of a volatile liquid (or gas) in a liquid is directly proportional to its mole fraction.

$P \propto x \Rightarrow P = K_H x$ (K_H = Henry's constant)

If we compare both equation, we can say that those are very similar and it seems that Raoult's law is a special case of Henry's law. When $K_H = P°$.

23. **Raoult's law :** For a solution of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction. Thus, for any component, partial vapour pressure, $p \propto x \Rightarrow p = p°.\ x$
where, $p°$ = vapour pressure of pure component
x = mole fraction of that component
Let a solution consists of two volatile liquids A and B with their mole fractions x_A and x_B respectively. If p_A and p_B are their partial vapour pressures,
then, $p_A \propto x_A \Rightarrow p_A = p_A^\circ x_A$ and $p_B \propto x_B \Rightarrow p_B = p_B^\circ x_B$
where p_A° and p_B° represent the vapour pressures of pure liquid components A and B. $P_{total} = p_A + p_B$
Ideal solutions obey Raoult's law at all concentrations and temperature.

24. **(c):** *n*-Hexane and *n*-heptane will form an ideal solution.

25. A solution which obeys Raoult's law of vapour pressure for all compositions is called ideal solution.

For ideal solution $\Delta V_{mix} = 0, \Delta H_{mix} = 0$
$A—B$ interaction = $A—A$ and $B—B$ interactions.

26. (a) The differences between ideal solutions and non ideal solutions are as follows :
(i) In ideal solutions $\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$ whereas in non-ideal solutions,

$$\Delta V_{mix} \neq 0 \text{ and } \Delta H_{mix} \neq 0.$$

(ii) In ideal solutions, each component obeys Raoult's law at all temperatures and concentrations whereas in non ideal solutions, they do not obey Raoult's law.
(b) Given, weight of urea (W_2) = 30 g
Weight of water (W_1) = 846 g
Vapour pressure of water p_1° = 23.8 mm Hg

$$n_B = \frac{30}{60} = 0.5,\ n_A = \frac{846}{18} = 47$$

$$\text{Mole fraction of water } (x_A) = \frac{n_A}{n_A + n_B}$$

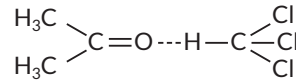
$$= \frac{47}{47 + 0.5} = \frac{47}{47.5} = 0.99$$

$p_A = p_A^\circ \times x_A = 23.8 \times 0.99 = 23.5$ mm Hg

27. **(a):** Acetone and chloroform form H-bonding due to which molecules come closer to each other and the volume of solution decreases.

28. A mixture of ethanol and acetone shows positive deviation from Raoult's law. When acetone is added to ethanol, some of the H-bonds between the ethanol molecules break down resulting in an increase in the vapour pressure of the mixture.

29. Mixture of chloroform and acetone shows negative deviation from Raoult's law, thus it forms maximum boiling azeotrope. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown :



This decreases the escaping tendency of molecules of each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law.

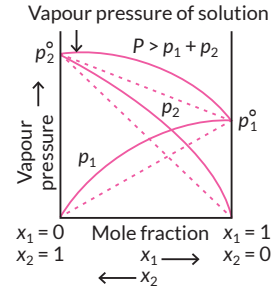
30. The differences between ideal solutions and non ideal solutions are as follows :
(i) In ideal solutions $\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$ whereas in non ideal solutions, $\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$.

(ii) In ideal solutions, each component obeys Raoult's law at all temperatures and concentrations whereas in non ideal solutions, they do not obey Raoult's law.

31. **Positive deviation :** For non-ideal solutions, if the vapour pressure is higher, than as expected from Raoult's law then it is said to exhibit positive deviation.

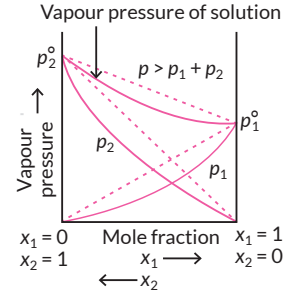
$A—B$ interactions are weaker than $A—A$ or $B—B$ interactions. Due to this, vapour pressure increases which results in positive deviation.

In positive deviation, intermolecular force decreases, volume increases, vapour pressures increases. enthalpy increases. Therefore, ΔH_{mix} = +ve, ΔV_{mix} = + ve. *e.g.*, ethanol + acetone and carbon disulphide + acetone show positive deviation.



Plot for non-ideal solution showing positive deviation

Negative deviation : For non-ideal solution, if the vapour pressure is lower than as expected from Raoult's law, then it is said to exhibit negative deviation. $A—B$ interactions are stronger than $A—A$ and $B—B$ interactions. Due to this, vapour pressure decreases which results in negative deviation. In negative deviation, intermolecular force increases, volume decreases, vapour pressure decreases and heat is released. Therefore, ΔH_{mix} = – ve, ΔV_{mix} = – ve. For example, phenol + aniline and chloroform + acetone show negative deviation.



Plot for non-ideal solution showing negative deviation

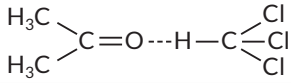
32. A mixture of ethanol and acetone shows positive deviation from Raoult's law. Pure ethanol possesses hydrogen bonding. Introduction of acetone between the molecules of ethanol results in breaking of some of these hydrogen bonds. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

33. **(a):** Solutions which show positive deviation from Raoult's law are minimum boiling azeotropes or have a lower boiling point than either of the two components.

34. Non-ideal solutions that show negative deviation from Raoult's law form maximum boiling azeotropes.

35. Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phase and boil at constant temperature.

36. Mixture of chloroform and acetone shows negative deviation from Raoult's law, thus it forms maximum boiling azeotrope. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown:



This decreases the escaping tendency of molecules of each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law.

37. Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phase and boil at constant temperature.
A minimum boiling azeotrope is formed by solutions showing a large positive deviation from Raoult's law at a specific composition. For example an ethanol-water mixture containing approximately 95% ethanol by volume.

38. Azeotropes are the binary mixtures of solutions that have the same composition in liquid and vapour phase and boil at constant temperature.
A maximum boiling azeotrope is formed by solutions showing a large negative deviation from Raoult's law at a specific composition.
For example, chloroform + acetone mixture.

39. The properties which depend upon the number of solute particles irrespective of their nature relative to the total number of particles present in the solution are called colligative properties.

40. When a non-volatile solute is added to a solvent, the vapour pressure of the solvent decreases as compared to the vapour pressure of pure solvent.

41. $W_2 = 10$ g, $W_1 = 200$ g, $T = 308$ K
$P_A^\circ = 32$ mm Hg, $P_S = 31.84$ mm Hg, $M_1 = 18$, $M_2 = ?$

$$\frac{P_A^\circ - P_S}{P_A^\circ} = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} \quad \text{(Solution is very dilute, } n_1 + n_2 \approx n_1\text{)}$$

$$\frac{32 - 31.84}{32} = \frac{10 \times 18}{M_2 \times 200}$$

$M_2 = 180$

42. (a) In osmotic pressure method, pressure can be measured at room temperature and the molarity of the solution is used instead of molality. That is why this method is used for determination of molar masses of macromolecules such as proteins as they are generally not stable at higher temperatures and polymers have poor solubility.
(b) Increase in temperature decreases the solubility of oxygen in water. As a result, amount of dissolved oxygen decreases. It becomes more difficult to breathe as oxygen is less. Hence, the aquatic species are not comfortable in warm water.

(c) i for 1 M KCl = 2
i for sugar solution = 1
$\therefore \Delta T_b = iK_b m = 2K_b$ (for KCl)
$\Delta T_b = K_b$ (for sugar)
$\therefore$ ΔT_b of 1 M KCl solution is double than that of 1 M sugar solution.

43. Given, $P_s^\circ = 17.536$ mm, $P_s = ?$,
$w_2 = 20$ g, $M_2 = 180$ g mol^{-1}, $w_1 = 500$ g, $M_1 = 18$ g

$$\frac{P_s^\circ - P_s}{P_s^\circ} = x_2 = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$$

$$\frac{17.536 - P_s}{17.536} = \frac{\frac{20}{180}}{\frac{500}{18} + \frac{20}{180}} \approx \frac{\frac{20}{180}}{\frac{500}{18}} \qquad \left(\because \frac{20}{180} <<< \frac{500}{18}\right)$$

$$(17.536 - P_s) = \frac{20}{180} \times \frac{18}{500} \times 17.536 = 0.070$$

$P_s = 17.536 - 0.070 = 17.466$ mm

Concept Applied

➲ Relative lowering of vapour pressure of a solution is equal to mole fraction of solute, *i.e.*, $\frac{p^\circ - p_S}{p^\circ} = X_B$.

44. Given, weight of urea (W_2) = 30 g
Weight of water (W_1) = 846 g
Vapour pressure of water $p_1^\circ = 23.8$ mm Hg

$$n_B = \frac{30}{60} = 0.5, \quad n_A = \frac{846}{18} = 47$$

$$\text{Mole fraction of water } (x_A) = \frac{n_A}{n_A + n_B} = \frac{47}{47 + 0.5} = \frac{47}{47.5} = 0.99$$

$p_A = p_A^\circ \times x_A = 23.8 \times 0.99 = 23.5$ mm Hg

45. (a) Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.
$p = K_H \cdot x$ where, K_H = Henry's law constant. Different gases have different K_H values at the same temperature.
Applications of Henry's law :
(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
(ii) To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.
(b) Given, $w_2 = 5$ g, $w_1 = 95$ g, $P_s = 745$ mm
$P_s^\circ = 760$ mm, $M_2 = ?$

$$\frac{P_s^\circ - P_s}{P_s^\circ} = x_2 = \frac{n_2}{n_1 + n_2} = \frac{w_1/M_2}{w_1/M_1 + w_2/M_2}$$

$$\frac{760 - 745}{760} = \frac{5/M_2}{95/18 + 5/M_2} = \frac{5/M_2}{95/18} \qquad \left(\because \frac{95}{18} >>> \frac{5}{M_2}\right)$$

$$\frac{15}{760} \times \frac{95}{18} = \frac{5}{M_2}$$

$$\Rightarrow \quad M_2 = \frac{5 \times 760 \times 18}{15 \times 95} = 48 \text{ g mol}^{-1}$$

46. (c): $\Delta T_b = K_b \times m$
$T_b - T_b^\circ = 0.52 \times 0.2 \Rightarrow T_b = 0.104 + T_b^\circ$
$T_b = (0.104 + 100)\,°C = 100.104\,°C$

47. (c): Assertion is correct but reason is wrong as elevation in boiling point is directly proportional to molality not molarity.
$\Delta T_b \propto m$
$\Delta T_b = K_b m$

48. Molal elevation constant may be defined as the elevation in boiling point when the molality of the solution is unity (*i.e.*, 1 mole of the solute is dissolved in 1 kg (1000 g) of the solvent). The units of K_b are therefore, K/m or °C/m or K kg mol^{-1}.

49. The boiling point of the solution is always higher than that of the pure solvent. As the vapour pressure of the solution is lower than that of the pure solvent and vapour pressure increases with increase in temperature, hence, the solution has to be heated more to make the vapour pressure equal to the atmospheric pressure.
Elevation of boiling point is a colligative property because it depends on number of solute particles present in a solution.

50. (d): *X* represents freezing point of solution.

51. Molality (m) of urea $= \frac{7.5\times1000}{60\times100} = 1.25$ m ...(i)
Molality of substance,

$$Z = \frac{42.75\times1000}{\text{Molar mass}\times100} = \frac{427.5}{\text{Molar mass}} \quad \text{...(ii)}$$

As both the solutions have same depression in freezing point so they have same molality.
From eqn. (i) and (ii), we get

$$1.25 = \frac{427.5}{\text{Molar mass}}$$

Molar mass of Z = 342 g/mol

52. Mass of glucose ($C_6H_{12}O_6$), W_2 = 60 g
Mass of water, W_1 = 250 g
M_2 (Mol. mass of $C_6H_{12}O_6$) = 180 g mol^{-1}
K_f = 1.86 K kg mol^{-1}, T_f = ?

Using formula, $\Delta T_f = K_f \times \frac{W_2\times1000}{M_2\times W_1} = 1.86\times\frac{60\times1000}{180\times250}$ K

$\Delta T_f = T_f^\circ - T_f$ or $T_f = T_f^\circ - \Delta T_f = 273 - 2.48 = 270.52$ K

Key Points

- As there is depression in freezing point so,
  $T_f < T_f^\circ \quad \therefore \quad \Delta T_f = T_f^\circ - T_f = +ve$

53. Given : W_2 = ?, M_2 = 256 g mol^{-1}, ΔT_f = 0.48 K
W_1 = 75 g, K_f = 5.12 K kg mol^{-1}

$$\Delta T_f = \frac{K_f\times W_2\times1000}{M_2\times W_1}$$

$$W_2 = \frac{\Delta T_f\times M_2\times W_1}{K_f\times1000} = \frac{0.48\times256\times75}{5.12\times1000} = 1.8\text{ g}$$

54. Mass of ethylene glycol ($C_2H_6O_2$), W_2 = 31 g
Mass of water, W_1 = 600 g
M_2 (Mol. mass of $C_2H_6O_2$) = 62 g mol^{-1},
K_f = 1.86 K kg mol^{-1}, T_f = ?

Using formula, $\Delta T_f = K_f \times \frac{W_2\times1000}{M_2\times W_1} = 1.86\times\frac{31\times1000}{62\times600}$ K = 1.55 K

$\Delta T_f = T_f^\circ - T_f$ or $T_f = T_f^\circ - \Delta T_f = 273 - 1.55 = 271.45$ K

55. Given, M_2 = 176 g mol^{-1}, ΔT_f = 1.5°C
w_1 = 75 g, K_f = 3.9 K kg mol^{-1}, w_2 = ?

$$\Delta T_f = \frac{K_f\times w_2\times1000}{M_2\times w_1}$$

$$w_2 = \frac{\Delta T_f\times M_2\times w_1}{K_f\times1000} = \frac{1.5\times176\times75}{3.9\times1000} = 5.077\text{ g}$$

56. Molality of sucrose solution (m) $= \frac{w_2\times1000}{M_2\times w_1}$
$= \frac{4\times1000}{342\times96} = 0.121$ m
ΔT_f for sucrose solution = 273.15 – 271.15 = 2 K

$$K_f = \frac{\Delta T_f}{m} = \frac{2}{0.121} = 16.52\,K/m$$

Molality of glucose solution $= \frac{5\times1000}{180\times95} = 0.292$ m
$\Delta T_f = K_f \times m = 16.52 \times 0.292 = 4.82$ K
Freezing point of glucose solution = 273.15 – 4.82
= 268.33 K

57. W_2 = 1.00 g, W_1 = 50 g, K_f = 5.12 K kg mol^{-1}, ΔT_f = 0.40 K

$$\Delta T_f = \frac{K_f\times W_2\times1000}{M_2\times W_1}$$

$$M_2 = \frac{K_f\times W_2\times1000}{W_1\times\Delta T_f} = \frac{5.12\times1\times1000}{50\times0.40} = 256\text{ g mol}^{-1}$$

58. Molality of sugar solution
$= \frac{W_2\times1000}{M_2\times W_1} = \frac{5}{342}\times\frac{1000}{95} = 0.154$ m

$\Delta T_f = T_f^\circ - T_f = 273.15 - 271 = 2.15$ K

$\Delta T_f = K_f \times m \quad \therefore \quad K_f = \frac{\Delta T_f}{m} = \frac{2.15}{0.154}$

Molality of glucose solution
$= \frac{W_2\times1000}{M_2\times W_1} = \frac{5}{180}\times\frac{1000}{95} = 0.292$ m

$\therefore \quad \Delta T_f$ (Glucose) $= K_f \times m = \frac{2.15}{0.154}\times0.292 = 4.08$ K

$\therefore$ Freezing point of glucose solution = 273.15 – 4.08
= 269.07 K

59. Molality (m) of sucrose solution
$= \frac{w_2\times1000}{M_2\times w_1} = \frac{10}{342}\times\frac{1000}{90} = 0.325$ m

ΔT_f for sucrose solution $= T_f^\circ - T_f = (273.15 - 269.15)$ K = 4 K

$\therefore \quad K_f = \frac{\Delta T_f}{m} = \frac{4\text{ K}}{0.325\text{ m}} = 12.308$ K/m $\because \Delta T_f = K_f \times m$

Molality of glucose solution $= \frac{10}{180}\times\frac{1000}{90} = 0.617$ m

$\Delta T_f = K_f \times m$
$\therefore \quad \Delta T_f = 12.308$ K/m $\times$ 0.617 m = 7.59 = 7.6 K

$\therefore$ Freezing point of glucose solution,

$T_f^\circ - \Delta T_f = (273.15 - 7.60)\ K = 265.55\ K$

60. Mass of ethylene glycol ($C_2H_6O_2$), $W_2 = 31$ g
Mass of water, $W_1 = 500$ g
M_2 (Mol. mass of $C_2H_6O_2$) = 62 g mol^{-1},
$K_f = 1.86$ K kg mol^{-1}, $T_f = ?$

Using formula, $\Delta T_f = K_f \times \frac{W_2 \times 1000}{M_2 \times W_1}$

$$= 1.86 \times \frac{60 \times 1000}{180 \times 250} K$$

$\Delta T_f = T_f^\circ - T_f$ or $T_f = T_f^\circ - \Delta T_f = 273 - 2.48 = 270.52 K$

61. $T_f = -15°C$, $K_f = 1.86$ K kg mol^{-1}

$\Delta T_f = T_f^\circ - T_f = 0 - (-15°C) = 15°C$

$\Delta T_f = K_f \times m$

$$15 = 1.86 \times \frac{\text{Number of moles of solute}}{5}$$

$\Rightarrow$ Number of moles of solute = 40.32 moles

$\Delta T_b = K_b \times m$

$$\Delta T_b = 0.52 \times \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

$$\Delta T_b = 0.52 \times \frac{40.32}{5\,kg} = 4.19$$

$\Delta T_b = T_b - T_b^\circ \Rightarrow 4.19 = T_b - 373$

$T_b = 373 + 4.19 = 377.19$ K

Key Points

- Same moles of solute are used here for the calculation of boiling point and freezing point.

62. (a): In osmotic pressure method, pressure can be measured at room temperature and the molarity of the solution is used instead of molality. That is why this method is used for determination of molar masses of macromolecules such as proteins as they are generally not stable at higher temperatures and polymers have poor solubility.

63. (c): A raw mango shriveled into pickle due to osmosis.

64. (a): Colligative properties of ideal solutions depend only on the number of particles of solute dissolved in a definite amount of the solvent and do not depend on the nature of solute.

Answer Tips

- $\pi = CRT$ where C is Molarity.

65. When the external pressure applied becomes more than the osmotic pressure of solution then the solvent molecules from the solution pass through the semi-permeable membrane to the solvent side and the process is called reverse osmosis.

66. In osmotic pressure method, pressure can be measured at room temperature and the molarity of the solution is used instead of molality. That is why this method is used for determination of molar masses of macromolecules such as proteins as they are generally not stable at higher temperatures and polymers have poor solubility.

67. Osmotic pressure is the extra pressure which is applied on the solution to prevent the flow of solvent into the solution through a semi-permeable membrane.

68. Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

69. Molarity (M) of urea solution

$$= \frac{w \times 1000}{M \times \text{Volume of solvent (mL)}} = \frac{5 \times 1000}{60 \times 100} = 0.833\,M$$

Osmotic pressure (π) = CRT = 0.833 × 0.0821 × 300
= 20.51 atm

70. (a) When we cook the food inside the pressure cooker, high pressure is created inside the cooker. Pressure will increase so, the boiling point will increase. Thus, cooking is faster in pressure cooker than in cooking pan.

(b) When red blood cells (RBC) are placed in saline water, water will flow out of the cells (low conc. to high conc.) and they would shrink. Such a solution is called hypertonic. On the other hand when red blood cells (RBC) are placed in distilled water, water will flow into the cell and they would swell. Such solution is called hypotonic.

71. (i) The elevation in boiling point of a solution is a colligative property which depends on the number of moles of solute added. Higher the concentration of solute added, higher will be the elevation in boiling point. Thus, 2 M glucose has higher boiling point than 1 M glucose solution.

(ii) When the external pressure applied becomes more than the osmotic pressure of solution then the solvent molecules from the solution pass through the semi-permeable membrane to the solvent side and the process is called reverse osmosis.

72. (i) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution exosmosis takes place that results in shrinking of cells.

(ii) 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells thus, on placing blood cells in this solution endosmosis takes place that results in swelling of cells.

Concept Applied

- **Exosmosis :** The outward flow of solvent (water) from the cell when placed in more concentrated solution (hypertonic). Cell shrinks in this case.
- **Endosmosis :** The inflow of solvent (water) into a cell from outside when cell is placed in distilled water. Cell swells up in this case.

73. $\pi = cRT$, $c = \frac{w_2}{M_2 \times V}$

w_2 = weight of solute
M_2 = molar mass of solute

$\frac{\pi_1}{\pi_2} = \frac{c_1 RT_1}{c_2 RT_2}$. Given, $T_1 = T_2$

$$\frac{\pi_1}{\pi_2}=\frac{c_1}{c_2}\Rightarrow\frac{4.98}{1.52}=\frac{\frac{30}{180\times1}}{c_2}\Rightarrow c_2=\frac{30\times1.52}{180\times4.98}=0.051\text{ mol/L}$$

74. Mass of urea = 15 g
Molar mass of urea = 60 g mol^{-1}
Molar mass of glucose = 180 g mol^{-1}
Mass of glucose = ?
For isotonic solution, osmotic pressure, $\pi_{1(urea)} = \pi_{2(glucose)}$
$n_1 = n_2$ (when volume is same)

or $\frac{W_1}{M_1}=\frac{W_2}{M_2}\Rightarrow\frac{15}{60}=\frac{W_2}{180}\Rightarrow W_2=\frac{15\times180}{60}=45\text{ g}$

Answer Tips

- $\pi = cRT = \frac{n}{V\text{ (in L)}}RT = \frac{W}{M\times V\text{ (in L)}}\times RT$

75. (i) Osmotic pressure is the extra pressure which is applied on the solution to prevent the flow of solvent into the solution through a semi-permeable membrane.
(ii) Properties which depend upon the number of solute particles irrespective of their nature relative to the total number of particles present in the solution are called colligative properties.

76. **van't Hoff factor :** It is defined as the ratio of the experimental value of colligative property to the calculated value of the colligative property and is used to find out the extent of dissociation or association. Mathematically, it is represented as

$$i=\frac{\text{Experimental (or observed) value of colligative property}}{\text{Calculated (or normal) value of colligative property}}$$

77. The molar mass which is either lower or higher than the expected or normal value is known as abnormal molar mass.

78. (a) When $i > 1$, solute is in dissociated state in the solution.
(b) When $i < 1$, solute is in associated state in the solution.

79. **van't Hoff factor :** It is defined as the ratio of the experimental value of colligative property to the calculated value of the colligative property and is used to find out the extent of dissociation or association. Mathematically, it is represented as

$$i=\frac{\text{Experimental (or observed) value of colligative property}}{\text{Calculated (or normal) value of colligative property}}$$

(i) van't Hoff factor (i) > 1 for solutes undergoing dissociation
(ii) van't Hoff factor (i) < 1 for solutes undergoing association

80. i for 1 M KCl = 2
i for sugar solution = 1
$\therefore\quad \Delta T_b = iK_b m = 2\,K_b$ (for KCl)
$\Delta T_b = K_b$ (for sugar)
$\therefore\quad \Delta T_b$ of 1 M KCl solution is double than that of 1 M sugar solution.

81. (i) As KCl is an electrolyte and one formula unit of KCl dissociates to give two ions (K^+ and Cl^-), therefore molar concentration of particles in the solution = 0.1 × 2 M = 0.2 M
As elevation of boiling point (or any colligative property) is directly proportional to number of particles in solution, hence 0.1 M KCl has higher boiling point than that 0.1 M glucose.
(ii) Salting is used because most bacteria, fungi and other potentially pathogenic organisms cannot survive in a highly salty environment, due to the hypertonic nature of salt. Any living cell in such an environment will become dehydrated through osmosis and die or become temporarily deactivated.

Key Points

- High concentration of salt - Hypertonic
- Low concentration of salt - Hypotonic

82. (a) i for 0.1 m KCl = 2
i for 0.1 m glucose = 1
$\therefore\quad \Delta T_b = i\,K_b m = 2K_b \times 0.1$ (for KCl)
$\Delta T_b = 1K_b \times 0.1$ (for glucose)
Thus, ΔT_b for KCl will be higher than for glucose solution as KCl will undergo dissociation and i is greater than 1.
(b) (i) i will be greater than 1 when CH_3COOH is dissolved in water as it undergoes dissociation.

$$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$$

(ii) i will be less than 1 when CH_3COOH is dissolved in benzene as it undergoes association.

$$2CH_3COOH \xrightarrow{\text{benzene}} (CH_3COOH)_2 \quad \text{(Dimerisation)}$$

83. Mass of $CaCl_2$ (W_2) = 10 g
Mass of water (W_1) = 200 g
Molar mass of $CaCl_2$ (M_2) = 111 g mol^{-1}
Molal elevation constant (K_b) = 0.52 K kg mol^{-1}

$$m=\frac{W_2\times1000}{M_2\times W_1}\quad\Rightarrow\quad m=\frac{10}{111}\times\frac{1000}{200}=0.450\text{ m}$$

$\Delta T_b = iK_b m = 3 \times 0.52 \times 0.450 = 0.702$ K

84. $W_2 = 4$ g, $M_2 = 120$ g mol^{-1}
$W_1 = 100$ g, $K_b = 0.52$ K kg mol^{-1}
For complete dissociation, $i = 2$
Using formula, $\Delta T_b = iK_b m$

or $\Delta T_b=\frac{i\times K_b\times W_2\times1000}{M_2\times W_1}=2\times0.52\times\frac{4\times1000}{120\times100}=0.34\text{ K}$

$\therefore\quad T_b = T_b^\circ + \Delta T_b = 100 + 0.34 = 100.34°C$

85. (i) The boiling point of 1M NaCl solution is more than that of 1M glucose solution as the value of 'i', *i.e.*, van't Hoff factor is 2 for NaCl and it is 1 for glucose. Also,

$$\Delta T_b = i \times K_b \times m$$

Hence, from the above mathematical reaction, it is clear that the increase in boiling point will be more for NaCl than that of glucose.
(ii) Let $p°$ be the vapour pressure of pure benzene. The vapour pressure of the solution will be $\frac{90}{100}p^\circ = 0.9p^\circ$.
Molar mass of solute (M_2) and benzene (M_1) are 50 g mol^{-1} and 78.1 g mol^{-1} respectively. Mass of benzene (w_1) is 78 g.

$$\frac{p^\circ-p}{p^\circ}=\frac{w_2}{M_2}\times\frac{M_1}{w_1}$$

$$\frac{p^\circ - 0.9p^\circ}{p^\circ} = \frac{w_2}{50} \times \frac{78.1}{78}$$

$\Rightarrow w_2 = 5$ g

Thus, the mass of *X* dissolved in the solution is 5 g.

(iii) It is given that $MgCl_2$ is completely dissociated in the solution.

$$MgCl_{2(s)} \xrightarrow{(aq)} Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

$\therefore$ $i = 3, w_B = 10$ g; $w_A = 200$ g $= 0.2$ kg

$K_b = 0.512$ K kg mol^{-1}

$$\Delta T_b = i \times K_b \times m = \frac{i \times K_b \times w_B}{M_B \times w_A}$$

$$\Delta T_b = \frac{(3) \times (0.512\,\text{K kg mol}^{-1}) \times (10\text{g})}{(95\,\text{g mol}^{-1}) \times (0.2\,\text{kg})} = 0.80\,\text{K}$$

86. (d): $NaCl \longrightarrow Na^+ + Cl^-$ $\quad i = 2$

$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$ $\quad i = 3$

$C_6H_{12}O_6$ (non-ionisable) $\quad i = 1$

$Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-}$ $\quad i = 5$

Greater the number of ions produced on dissociation, greater is the van't Hoff factor.

$\because$ $\Delta T_f \propto i$

$\therefore$ $Al_2(SO_4)_3$ shows largest freezing point depression.

87. Molecular mass of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$)

$= [2 \times 23 + 32 + 16 \times 4 + 10 \times (2 \times 1 + 16)]$

$= (46 + 32 + 64 + 180)$ g mol^{-1} $= 322$ g mol^{-1}

$Na_2SO_4 \cdot 10H_2O$ ionises as :

$Na_2SO_4 \cdot 10H_2O \rightleftharpoons 2Na^+ + SO_4^{2-} + 10H_2O$

$\Rightarrow$ $i = 3$

$$m = \frac{n_B}{W_A} = \frac{W_B}{M_B \times W_A} = \frac{6.00\,\text{g}}{322\,\text{g mol}^{-1} \times 0.1\,\text{kg}}$$

$= 0.186$ mol kg^{-1} $= 0.186$ m

Also, $\Delta T_f = i K_f \cdot m = 3 \times 1.86$ K m$^{-1} \times 0.186$ m $= 1.04$ K

$\Rightarrow$ $T_f = T_f^\circ - \Delta T_f$

$= (273 - 1.04)$ K $= 271.96$ K

88. Given : $W_2 = 19.5$ g, $W_1 = 500$ g, $K_f = 1.86$ K kg mol^{-1}

$\Delta T_{f(obs)} = 1.0$ K

$$\therefore \quad M_{2(obs)} = \frac{1000 \times K_f \times W_2}{W_1 \times \Delta T_{f(obs)}} = \frac{1000 \times 1.86 \times 19.5}{500 \times 1}$$

$= 72.54$ g mol^{-1}

$M_{2(cal)}$ for F—CH_2—COOH $= 78$ g mol^{-1}

$$i = \frac{M_{2(cal)}}{M_{2(obs)}} = \frac{78}{72.54} = 1.0753$$

	F—CH_2—COOH $\rightleftharpoons$	F—CH_2—COO^- +	H^+
Initial moles	C	0	0
Moles at eqm.	$C - C\alpha$	$C\alpha$	$C\alpha$

Total no. of moles $= C - C\alpha + C\alpha + C\alpha = C(1 + \alpha)$

$$i = \frac{C(1+\alpha)}{C} = 1 + \alpha$$

or $\alpha = i - 1 = 1.0753 - 1 = 0.0753 = 7.53\%$

Answer Tips

- Since ΔT is the difference between values of temperatures, it is independent of the unit it is measured in *i.e.*, $\Delta T = 1^\circ$C $= 1$ K.

89. Given, $W_2 = 5$ g, $M_2 = 122$ g mol^{-1}, $W_1 = 35$ g

$\Delta T_f = 2.94$ K, $K_f = 4.9$ K kg mol^{-1}

$$\Delta T_f = i K_f m = i \times K_f \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

or $\quad 2.94 = i \times 4.9 \times \frac{5 \times 1000}{122 \times 35}$ $\quad$ or $i = 0.512$

As $i < 1$, solute is associated.

	$2C_6H_5COOH \rightleftharpoons$	$(C_6H_5COOH)_2$
Initial moles	1	0
Moles at eqm.	$1 - \alpha$	$\alpha/2$

Total no. of moles after association : $1 - \alpha + \alpha/2 = 1 - \alpha/2$

$$\therefore \quad i = \frac{1 - \alpha/2}{1} = 1 - \frac{\alpha}{2}$$

$$\Rightarrow \quad 1 - \frac{\alpha}{2} = 0.512$$

or $\quad \alpha = 2 \times (1 - 0.512) = 0.976$ or 97.6%

Concept Applied

- For association of solute, $i = 1 - \alpha + \frac{\alpha}{n}$

  here $n = 2$, so, $i = 1 - \frac{\alpha}{2}$

90. Given, $\Delta T_f = 0.068^\circ$C or 0.068 K

$m = 0.01$ M, $\quad K_f = 1.86$ K kg mol^{-1}

$\Delta T_f = iK_f \cdot m$

$\Rightarrow$ $0.068 = i \times 1.86 \times 0.01$

$$\Rightarrow \quad i = \frac{0.068}{1.86 \times 0.01} = 3.65$$

$AlCl_3$ dissociates as

	$AlCl_3 \rightleftharpoons$	Al^{3+} +	$3Cl^-$
Initially	1	0	0
At eqm.	$1 - \alpha$	α	3α

Total no. of moles after dissociation $= 1 - \alpha + \alpha + 3\alpha = 1 + 3\alpha$

$$i = \frac{1 + 3\alpha}{1} = 3.65$$

$\Rightarrow$ $1 + 3\alpha = 3.65 \Rightarrow 3\alpha = 3.65 - 1 = 2.65$

$$\Rightarrow \quad \alpha = \frac{2.65}{3} = 0.883$$

Percentage association $= 88.3\%$

91. $\Delta T_f = iK_f \cdot m$

i for $MgCl_2 = 3$

$$\text{Molality, } m = \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{1.9 \times 1000}{95 \times 50} = 0.4\ \text{m}$$

$\Delta T_f = 3 \times 1.86 \times 0.4 = 2.232$ K

Freezing point of solution, $T_f = T_f^\circ - \Delta T_f = 273 - 2.232$ K

$= 270.77$ K

92. $W_2 = 2.56$ g, $W_1 = 100$ g, $\Delta T_f = 0.383$ K

$K_f = 3.83$ K kg mol^{-1}, $\Delta T_f = K_f \times m$

$$\Rightarrow \quad \Delta T_f = K_f \times \frac{W_2}{M_2} \times \frac{1000}{W_1} \Rightarrow M_2 = \frac{W_2 \times 1000}{\Delta T_f \times W_1} \times K_f$$

$$= \frac{2.56 \times 1000}{0.383 \times 100} \times 3.83 = 256\ \text{g mol}^{-1}$$

$\because \quad i = \dfrac{\text{Normal atomic mass}}{\text{Observed atomic mass}} = \dfrac{32}{256} = \dfrac{1}{8}$

Sulphur exists as S_x *i.e.*, S_8.

Concept Applied

➲ Value of observed atomic mass is used to calculate the value of x here.

93. $W_2 = 3.9$ g, $W_1 = 49$ g, $\Delta T_f = 1.62$ K, $M_2 = 122$ g mol^{-1}, $K_f = 4.9$ K kg mol^{-1}

$$\Delta T_f = i K_f m = i \times K_f \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$\Rightarrow \quad 1.62 = \frac{i \times 4.9 \times 3.9 \times 1000}{122 \times 49} \Rightarrow i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.506$$

As $i < 1$, solute is associated.

94. $\Delta T_f = iK_f m = \dfrac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$

$$2 = \frac{2 \times 1.86 \times W_2 \times 1000}{58.5 \times 37.2} \Rightarrow W_2 = 1.17 \text{ g}$$

95. (a) The differences between ideal solutions and non-ideal solutions are as follows :

(i) In ideal solutions $\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$ whereas in non ideal solutions, $\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$.

(ii) In ideal solutions, each component obeys Raoult's law at all temperatures and concentrations whereas in non ideal solutions, they do not obey Raoult's law.

(b) $\Delta T_f = iK_f m = \dfrac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$

$$2 = \frac{2 \times 1.86 \times W_2 \times 1000}{58.5 \times 100} \Rightarrow W_2 = 3.145 \text{ g}$$

96. (a) The two characteristics of non-ideal solution are :

(i) They do not obey Raoult's law over the entire range of concentration.

(ii) The vapour pressure of non-ideal solution is either higher or lower than that predicted by Raoult's law.

(b) Given, $w_2 = 2$ g, $M_2 = 122$ g mol^{-1}, $w_1 = 25$ g,

$\Delta T_f = 1.62$ K, $K_f = 4.9$ kg mol^{-1}

$\Delta T_f = i K_f m$

$$1.62 = i \times 4.9 \times \frac{2}{122 \times 25} \times 1000$$

$$\Rightarrow \quad i = \frac{1.62 \times 122 \times 25}{4.9 \times 2 \times 1000} = 0.5042$$

$$\alpha_{association} = \frac{1 - i}{1 - \frac{1}{n}} = \frac{1 - 0.5042}{1 - \frac{1}{2}} = 0.4958 \times 2 = 0.9916$$

% of association = 0.9916 × 100 = 99.16%

97. $\pi = iCRT = i \cdot \dfrac{n}{V} RT = i \times \dfrac{w}{M} \times \dfrac{1}{V} RT$

or $\quad 4.75 = i \times \dfrac{5.85}{58.5} \times \dfrac{1}{1} \times 0.082 \times 300$ or $i = 1.93$

$$NaCl \longrightarrow Na^+ + Cl^-$$

Initial moles	C	0	0
Moles at eqm.	$C - C\alpha$	$C\alpha$	$C\alpha$

Total no. of moles = $C(1 + \alpha)$

$$i = \frac{C(1+\alpha)}{C} \text{ or } i = 1 + \alpha \text{ or } 1 + \alpha = 1.93$$

or $\quad \alpha = 0.93$ or 93%

Concept Applied

➲ For dissociation, $i = 1 - \alpha + x\alpha + y\alpha$
for NaCl, $x = 1$, $y = 1$ so, $i = 1 + \alpha$

98. Given : $\alpha = 95\%$, $C = 0.1$ M, $T = 27°C = 300$ K,

$R = 0.0821$ L atm K^{-1} mol^{-1}

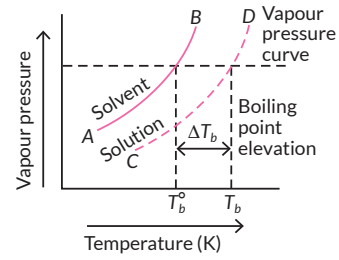
For Na_2SO_4, $\alpha_{dissociation} = \dfrac{i-1}{n-1}$

$$\frac{95}{100} = \frac{i-1}{3-1} \Rightarrow i = 2.9$$

$\pi = i\,CRT$

$\pi = 2.9 \times 0.1 \times 0.0821 \times 300 = 7.14$ atm

99. (a) Let T_b° is the boiling point of pure solvent and T_b is the boiling point of solution. The increase in the boiling point, $\Delta T_b = T_b - T_b^\circ$ is known as elevation of boiling point.



(b) Given, $W_2 = 25$ mg $= 25 \times 10^{-3}$ g

$M_2 = (2 \times 39) + 32 + (4 \times 16) = 174$ g mol^{-1},

$i = 3$, $V = 2$L, $T = 25°C = 25 + 273 = 298$ K

$$\pi = i\,CRT = 3 \times \frac{25 \times 10^{-3}}{174 \times 2} \times 0.0821 \times 298 = 5.27 \times 10^{-3} \text{ atm}$$

100. (i) The value of van't Hoff factor for ethanoic acid in benzene is close to 0.5 as two molecules of ethanoic acid associate to form a dimer in benzene solution.

$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

$$i = \frac{\text{Number of solute particles in solution}}{\text{Theoretical number of solute particles}}$$

$$= \frac{1}{2} = 0.5$$

(ii) It has been given that K_2SO_4 is completely dissociated. When K_2SO_4 is dissolved in water, K^+ and SO_4^{2-} ions are produced as shown:

$$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$$

Total number of ions produced = 3

$\therefore \quad i = 3$

Given,

$w = 2.32 \times 10^{-2}$ g; $V = 2$ L; $R = 0.082$ L atm K^{-1} mol^{-1}

$T = 25°C = (25 + 273)$ K $= 298$ K

Molar mass of $K_2SO_4 = (2 \times 39) + (1 \times 32) + (4 \times 16)$

$= 174$ g mol^{-1}

Applying the following relation,

$$\pi = i \frac{n}{V} RT$$

$$= i \times \frac{w}{M} \times \frac{1}{V} RT$$

$$= 3 \times \frac{2.32 \times 10^{-2}}{174} \times \frac{1}{2} \times 0.082 \times 298$$

$$= 4.8 \times 10^{-3} \text{ atm}$$

(iii) $\Delta T_f = iK_f m$

$$\Rightarrow \quad 0.512 = \frac{i \times 5.12 \times 25.6 \times 1000}{32 \times 1000}$$

$$\Rightarrow \quad i = \frac{0.512 \times 32 \times 1000}{5.12 \times 25.6 \times 1000}$$

$$i = \frac{1}{8} = 0.125$$

As '*i*' is less than 1, therefore S is associated, *i.e.*, 8 moles of S are associated as shown $8S \leftrightarrow S_8$.
Therefore, the molecular formula of sulphur is S_8.

CBSE Sample Questions

1. (c): Molarity is a mean to express concentration of solution. It is not a colligative property. **(0.77)**

2. (b): According to Le-Chatelier principle, solubility of gases in liquids decreases with rise in temperature because dissolution is an exothermic and reversible process. **(0.77)**

3. (b): Aquatic species are more comfortable in cold water rather than in warm water because the amount of dissolved oxygen in water decreases with rise in the water's temperature. **(1)**

4. (a) Henry's law : The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution. **(1)**

$p = K_H x$

The pressure underwater is high, so the solubility of gases in blood increases. When the diver comes to surface, the pressure decreases and so does the solubility, causing bubbles of nitrogen in blood. To avoid this situation and maintain the same partial pressure of nitrogen underwater too, the dilution is done. **(1)**

(b) Using equation $p = K_H \times x$

Mole fraction of argon in water, $x = p/K_H = 6/40 \times 10^3$

$= 1.5 \times 10^{-4}$ **(1)**

5. (b): Raoult's law **(0.77)**

6. (c): Let y_B be mole fraction of benzene in vapour phase.
y_T = Mole fraction of toluene in vapour phase.

$$y_{Benzene} = \frac{p_{Benzene}}{p_{Total}} ; y_{Toluene} = \frac{p_{Toluene}}{p_{Total}}$$

$p_{Benzene} = p^\circ_{Benzene} (x_{Benzene})$, $p_{Toluene} = p^\circ_{Toluene} (x_{Toluene})$

Since, $p^\circ_{Benzene} > p^\circ_{Toluene}$, $p_{Benzene} > p_{Toluene}$

Hence, $y_{Benzene} > y_{Toluene}$ **(1)**

7. (b): Nitric acid and water form maximum boiling azeotrope because they show large deviation from Raoult's law due to hydrogen bonding. **(1)**

8. (a): Fluid inside blood cells is isotonic with 0.9% NaCl solution. Hence, it will shrink when placed in water containing more than 0.9% (mass/volume) NaCl solution. **(0.77)**

9. (a): $\Delta T_f = T_f^\circ - T_f = 0 - (-14) = 14°C$, $\Delta T_f = K_f m$

$$\Delta T_f = K_f \times \frac{n_2 \times 1000}{w_1}$$

$$14 = 1.86 \times \frac{n_2 \times 1000}{1000} \Rightarrow n_2 = 7.5 \text{ mol} \quad \textbf{(0.77)}$$

10. (c) **(0.77)**

11. (c): Cryoscopic constant varies with type of solvent hence is not a universal constant. **(1)**

12. Given : $K_b = 0.52$ K kg mol^{-1}, boiling point of glucose, $\Delta T_b = 101.04°C$
As $\Delta T_b = T_b - T_b^\circ = 101.04°C - 100°C = 1.04°C$
$\Delta T_b = K_b m$

$$m = \frac{\Delta T_b}{K_b} = \frac{1.04}{0.52} = 2 \quad \textbf{(1)}$$

According to Raoult's law,
Relative lowering of vapour pressure = x_B
where x_B is mole fraction of solute.
Moles of glucose, $n_2 = 2$

$$\text{Moles of water, } n_1 = \frac{1000}{18} = 55.56$$

$$\therefore \quad \text{Relative lowering of vapour pressure} = \frac{n_2}{n_2 + n_1} \quad \textbf{(1/2)}$$

$$= \frac{2}{2 + 55.56} = \frac{2}{57.56} = 0.034 \quad \textbf{(1/2)}$$

13. The melting point of ice is the freezing point of water. We can use the depression in freezing point property in this case.
(a) In 3rd reading for 0.5 g, there has to be an increase in depression of freezing point and therefore, decrease in freezing point *i.e.*, decrease in melting point, when amount of salt is increased but the trend is not followed in this case. **(1)**
(b) Two sets of reading help to avoid error in data collection and give more objective data. **(1)**

(c) $$\Delta T_f \text{ (glucose)} = 1 \times K_f \times \frac{0.6 \times 1000}{180 \times 10}$$

$$\Delta T_f \text{ (NaCl)} = 2 \times K_f \times \frac{0.6 \times 1000}{58.5 \times 10}$$

$$\Rightarrow \quad 3.8 = 2 \times K_f \times \frac{0.6 \times 1000}{58.5 \times 10} \quad \textbf{(1)}$$

Dividing (i) by (ii)

$$\frac{\Delta T_f \text{ (glucose)}}{3.8} = \frac{58.5}{2 \times 180}$$

$$\Rightarrow \quad \Delta T_f = 0.62$$
$$\therefore \quad T_f = -0.62 °C \quad \textbf{(1)}$$

OR

Depression in freezing point is directly proportional to molality (mass of solute when the amount of solvent remains same).
0.3 g of salt causes depression of 1.9 °C.
0.6 g of salt causes depression of 3.8 °C.
1.2 g of salt causes depression of 3.8 × 2 = 7.6 °C. **(2)**

Self Assessment

Case Based Questions (5 marks)

1. **Read the passage given below and answer the following questions :**
The properties of the solutions which depend only on the number of solute particles but not on the nature of the solute are called colligative properties. Relative lowering in vapour pressure is also an example of colligative properties.
For an experiment, sugar solution is prepared for which lowering in vapour pressure was found to be 0.061 mm of Hg. (Vapour pressure of water at 20°C is 17.5 mm of Hg.)
(i) Relative lowering of vapour pressure for the given solution is
(a) 0.00348 (b) 0.061 (c) 0.122 (d) 1.75
(ii) The vapour pressure (mm of Hg) of solution will be
(a) 17.5 (b) 0.61 (c) 17.439 (d) 0.00348
(iii) Mole fraction of sugar in the solution is
(a) 0.00348 (b) 0.9965
(c) 0.061 (d) 1.75
(iv) If weight of sugar taken is 5 g in 108 g of water then molar mass of sugar will be
(a) 358 (b) 120 (c) 240 (d) 400
(v) The vapour pressure (mm of Hg) of water at 293 K when 25 g of glucose is dissolved in 450 g of water is
(a) 17.2 (b) 17.4 (c) 17.120 (d) 17.02

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

2. **Assertion :** The vapour pressure of 0.1 M sugar solution is less than 0.1 M $MgCl_2$ solution.
Reason : Lowering of vapour pressure is directly proportional to the number of species present in the solution.

3. **Assertion :** The relative lowering of vapour pressure for the $CH_3COOH - H_2O$ solution is more in comparison to $CH_3COOH - C_6H_6$.
Reason : Water is less volatile than benzene.

Multiple Choice Questions (1 mark)

4. 0.001 molal solution of $Pt(NH_3)_4Cl_4$ in water had a freezing point depression of 0.0054 °C. If K_f for water is 1.80, the correct formula of the compound is
(a) $[Pt(NH_3)_4Cl_3]Cl$ (b) $[Pt(NH_3)_4Cl_4]$
(c) $[Pt(NH_3)_4Cl_2]Cl_2$ (d) $[Pt(NH_3)_4Cl]Cl_3$

5. At high altitudes, the boiling point of water lowers because
(a) atmospheric pressure is low
(b) temperature is low
(c) atmospheric pressure is high
(d) none of these.

6. The correct order of increasing boiling point is
(a) 0.01 m $NaNO_3$ < 0.01 m $La(NO_3)_3$ < 0.01 m $MgBr_2$
(b) 0.01 m $NaNO_3$ < 0.01 m $MgBr_2$ < 0.01 m $La(NO_3)_3$
(c) 0.01 m $MgBr_2$ < 0.01 m $La(NO_3)_3$ < 0.01 m $NaNO_3$
(d) 0.01 m $La(NO_3)_3$ < 0.01 m $MgBr_2$ < 0.01 m $NaNO_3$.

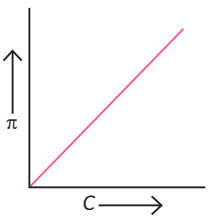
OR

In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is _____.
(a) the same (b) about twice
(c) about three times (d) about six times

VSA Type Questions (1 mark)

7. Why are soda water and soft drink bottles sealed under pressure?

8. A graph showing variation of osmotic pressure (π) *versus* molar concentration '*C*' of an aqueous solution at temperature *T* is given below. What does the slope of the line represents?



9. What are isotonic solutions?

10. Why does the freezing point of a solution decreases on adding non-volatile solute?

11. On what factor does the elevation in boiling point depend?

SA I Type Questions (2 marks)

12. Find the molality of a solution containing a non-volatile solute if the vapour pressure is 2% lower than the vapour pressure of pure water.

13. What will be the degree of dissociation of 0.1 M $Mg(NO_3)_2$ solution if van't Hoff factor is 2.74?

14. Define vapour pressure. What happens to the vapour pressure when (i) volatile solute dissolves in the liquid, (ii) non-volatile solute dissolves in the liquid?

15. Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

16. How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Explain the phenomenon involved in the process.

OR

Why is the vapour pressure of an aqueous solution of glucose lower than that of water?

SA II Type Questions (3 marks)

17. Why is it not possible to obtain pure ethanol by fractional distillation? What general name is given to binary mixtures which show deviation from Raoult's law and whose components cannot be separated by fractional distillation. How many types of such mixtures are there?

18. Calculate molarity and molality of a 13% solution (by weight) of sulphuric acid. Its density is 1.020 g cm^{-3}. (Atomic mass of H = 1, O = 16, S = 32 amu)

19. A 5% solution (*w*/*W*) of cane sugar (molar mass = 342 g mol^{-1}) has freezing point 271 K. What will be the freezing point of 5% glucose (molar mass = 180 g mol^{-1}) in water if freezing point of pure water is 273.15 K?

20. Arrange the depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid in increasing order. Explain briefly.

OR

Explain the terms ideal and non-ideal solutions in the light of forces of interactions operating between molecules in liquid solutions.

Case Based Questions (4 marks)

21. **Read the passage given below and answer the following questions :**

An ideal solution may be defined as the solution which obeys Raoult's law exactly over the entire range of concentration. The solutions for which vapour pressure is either higher or lower than that predicted by Raoult's law are called non-ideal solutions.

Non-ideal solutions can show either positive or negative deviations from Raoult's law depending on whether the *A*–*B* interactions in solution are stronger or weaker than *A* – *A* and *B* – *B* interactions.

(i) What type of solution is formed when chloroform is mixed with acetone?

(ii) What are the signs of ΔH and ΔV for a solution with positive deviation from ideal behaviour?

(iii) Name two factors on which the vapour pressure of a liquid depends.

OR

With suitable diagram and appropriate examples explain a non-ideal solution with negative deviation.

LA Type Questions (5 marks)

22. (i) When is the value of van't Hoff factor more than one?

(ii) An aqueous solution of glucose is made by dissolving 10 g of glucose ($C_6H_{12}O_6$) in 90 g of water at 303 K. If the vapour pressure of pure water at 303 K be 32.8 mm of Hg, what would be the vapour pressure of the solution?

(iii) With the help of a suitable diagram show that the lower vapour pressure of a solution than the pure solvent causes a lowering of freezing point for the solution compared to that of the pure solvent.

23. Calculate the osmotic pressure and the vapour pressure of 0.6% aqueous solution of non-volatile, non-electrolyte urea at 25 °C. The vapour pressure of pure water at 25°C is 24 mm of Hg. Take density to be 1 g mL^{-1} and assume ideal solution behaviour.

24. A solution of glucose in water is labelled as 20% (*w*/*W*). The density of the solution is 1.20 g mL^{-1}. Calculate

(i) molality (ii) molarity and

(iii) mole fraction of each component in solution.

25. (i) H_2S is a toxic gas used in qualitative analysis. If solubility of H_2S in water at NTP is 0.195 m, what is the value of K_H?

(ii) Define negative deviation from Raoult's law. Give an example of solution showing negative deviation from ideal behaviour.

(iii) What are minimum boiling azeotropes? Give an example.

OR

(i) What is the use of reverse osmosis?

(ii) 4% NaOH solution (mass/volume) and 6% urea solution (mass/volume) are equimolar but not isotonic. Why?

(iii) Name the colligative property mostly used for the determination of molecular mass of macromolecules.

(iv) What happens when RBCs are placed in

(a) 1% NaCl solution (b) pure water?

Detailed SOLUTIONS

1. (i) (a) : Vapour pressure of water (p_A°) = 17.5 mm of Hg
Lowering of vapour pressure ($p_A^\circ - p_A$) = 0.061 mm of Hg
Relative lowering of vapour pressure

$$= \frac{p_A^\circ - p_A}{p_A^\circ} = \frac{0.061}{17.5} = 0.00348$$

(ii) (c) : p_A = Vapour pressure of solvent – lowering in vapour pressure = 17.5 – 0.061 = 17.439 mm of Hg

(iii) (a): $\frac{p_A^\circ - p_A}{p_A^\circ} = x_B = 0.00348$

Hence, mole fraction of sugar = 0.00348

(iv) (c): $M_B = \dfrac{w_B M_A}{w_A\left(\dfrac{p_A^\circ - p_A}{p_A^\circ}\right)}$; $w_B = 5$ g, $M_A = 18$ g, $w_A = 108$ g

$$M_B = \frac{5\times 18}{108\times 0.00348} = 239.46 \approx 240\text{ g}$$

(v) (b): $\dfrac{p_A^\circ - p_A}{p_A^\circ} = x_B = \dfrac{w_B \times M_A}{M_B \times w_A}$

$$\frac{17.5 - p_A}{17.5} = \frac{25\times 18}{180\times 450} = 5.56\times 10^{-3}$$

$17.5 - p_A = 17.5 \times 5.56 \times 10^{-3}$

$17.5 - p_A = 0.0973$

$p = 17.40$ mm of Hg

2. (d): 0.1 M $MgCl_2$ contains more number of species in comparison to 0.1 M sugar, that's why $MgCl_2$ causes lower vapour pressure.

3. (b): CH_3COOH undergoes dimerisation in benzene causing decrease in effective number of species. Lesser the number of species in the solution, lesser the magnitude of colligative properties.

4. (c): $\Delta T_f = i \times K_f \times m$

$0.0054 = i \times 1.8 \times 0.001 \Rightarrow i = 3$

It gives 3 particles on dissociation. The correct formula of the molecule is $[Pt(NH_3)_4Cl_2]Cl_2$.

5. (a)

6. (b): ΔT_b being a colligative property depends upon the no. of solute particles *i.e.*, greater the no. of ions larger will be the elevation in boiling point and thus, greater will be the boiling point.

$La(NO_3)_3 \rightleftharpoons La^{3+} + 3NO_3^- \rightarrow 4$ ions

$MgBr_2 \rightleftharpoons Mg^{2+} + 2Br^- \rightarrow 3$ ions

$NaNO_3 \rightleftharpoons Na^+ + NO_3^- \rightarrow 2$ ions

$\therefore$ The correct order of increasing boiling point is 0.01 m $NaNO_3$ < 0.01 m $MgBr_2$ < 0.01 m $La(NO_3)_3$.

OR

(c) : 0.01 M solution of glucose does not ionise while 0.01 M $MgCl_2$ solution furnishes 3 ions ($Mg^{2+} + 2Cl^-$) in the solution, hence the value of colligative property for $MgCl_2$ solution is about 3 times.

7. To dissolve more CO_2, because solubility of CO_2 is high at higher pressure.

8. $\pi = CRT$

Comparing the above equation with $y = mx + c$

$y = \pi$, $x = C$, $m = RT$ = slope

9. Solutions having same osmotic pressure at given temperature are called isotonic solutions.

10. On adding non-volatile solute to a liquid its vapour pressure decreases, hence freezing point decreases.

11. Number of solute particles.

12. Given : $p_S = \left(\dfrac{98}{100}\right)p^\circ$

$$\frac{1}{x_B} - 1 = \frac{n_A}{n_B} \qquad \left[\because \frac{x_A}{x_B} = \frac{n_A}{n_B}\right]$$

$$\frac{p^\circ}{p^\circ - p_S} - 1 = \frac{n_A}{n_B} \Rightarrow \frac{p^\circ - (p^\circ - p_S)}{p^\circ - p_S} = \frac{n_A}{n_B} \Rightarrow \frac{p^\circ - p_S}{p_S} = \frac{n_B}{n_A}$$

$$\frac{p^\circ - p_S}{p_S} = \frac{W_B}{M_B}\times\frac{M_A}{W_A} = \frac{W_B}{M_B \times w_A}\times 1000 \times \frac{M_A}{1000}$$

$$\frac{p^\circ - (98/100)p^\circ}{(98/100)p^\circ} = \text{Molality} \times \frac{18}{1000}$$

$$\therefore \quad \text{Molality} = \frac{2p^\circ}{100\times\frac{98}{100}p^\circ}\times\frac{1000}{18} = 1.133 \text{ mol kg}^{-1}$$

13. $Mg(NO_3)_2 \longrightarrow Mg^{2+} + 2NO_3^-$

$$\alpha = \frac{i-1}{n-1} = \frac{2.74-1}{3-1} = \frac{1.74}{2} = 0.87$$

14. The pressure exerted by gaseous molecules on its liquid layer at equilibrium is called vapour pressure.

(i) When volatile solute is added to another liquid then the resultant vapour pressure may increase, decrease or may remain same depending on the strength of solute-solvent interaction.

(ii) Net vapour pressure decreases when non-volatile solute is added to it.

15. NaCl is a non-volatile solute hence it lowers the vapour pressure of water and boiling point of water increases. Methyl alcohol is a volatile solute hence it increases the vapour pressure and results in decrease in boiling point of water.

16. When salt is spread over snow covered roads, snow starts melting from the surface because of depression in freezing point of water and it helps in clearing the roads.

OR

When a non-volatile solute like glucose is dissolved in water, the solute molecules cover the portion of surface of the solution which prevents the molecules of water escaping from the surface in the form of vapours. Hence, the vapour pressure of the aqueous solution is reduced and is less than pure water.

17. Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes

(i) Minimum boiling azeotrope – The solutions which show positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

(ii) Maximum boiling azeotrope – The solutions which show negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.

18. Let mass of the solution = 100 g

Mass of the solute (w_2) = 13 g

and density of solution = 1.020 g cm^{-3}

Volume of the solution

$$= \frac{\text{Mass of the solution}}{\text{Density of solution}} = \frac{100\text{ g}}{1.020\text{ g cm}^{-3}} = \frac{100}{1.02}\text{ cm}^3$$

Molar mass of solute = $H_2SO_4 = 1 \times 2 + 32 + 16 \times 4$
$= 98 \text{ g mol}^{-1}$

Moles of the solute $= \frac{13}{98}\text{mol}$

Molarity $= \frac{\text{Moles of the solute}}{\text{Volume of solution in L}}$

$= \frac{13}{98} \times \frac{1000}{\frac{100}{1.02}} = \frac{13}{98} \times 1000 \times \frac{1.02}{100} = 1.353 \text{ M}$

Now, mass of solvent = 100 – 13 = 87 g

Molality $= \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{13}{98} \times \frac{1000}{87} = 1.52 \text{ m}$

19. $\Delta T_f = \frac{K_f \times W_B}{M_B \times W_A}$

For cane sugar solution, $2.15 = \frac{K_f \times 5}{342 \times 0.095}$

($\because$ 95 g of water = 0.095 kg)

For glucose solution, $\Delta T_f = \frac{K_f \times 5}{180 \times 0.095}$

$\frac{\Delta T_f}{2.15} = \frac{K_f \times 5}{180 \times 0.095} \times \frac{342 \times 0.095}{K_f \times 5}; \Delta T_f = \frac{342}{180} \times 2.15 = 4.085 \text{ K}$

Freezing point of glucose solution = 273.15 – 4.085
= 269.07 K

20. The depression in freezing point is in the order :
Acetic acid ($CH_3—COOH$) < trichloroacetic acid ($Cl_3C—COOH$) < trifluoroacetic acid ($F_3C—COOH$)
Fluorine, being most electronegative, has the highest electron withdrawing inductive effect. Consequently, trifluoroacetic acid is the strongest acid while acetic acid is the weakest acid. Hence, trifluoroacetic acid ionizes to the largest extent while acetic acid ionizes to the minimum extent to give ions in their solutions in water. Greater the ions produced, greater is the depression in freezing point. Hence, the depression in freezing point is the maximum for the fluoroacetic acid and minimum for acetic acid.

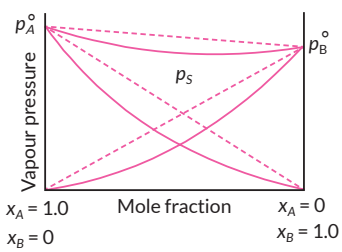
OR

Ideal solutions : The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. For an ideal solution, $\Delta_{mix}H = 0, \Delta_{mix}V = 0$
$A - B$ interactions $\approx A - A$ interactions and $\approx B - B$ interactions.
Non-ideal solutions : When solutions do not obey Raoult's law over the entire range of concentration, they are called non-ideal solutions.
Positive deviations : Vapour pressure of such solutions shows higher value than the predicted value.
$\Delta_{mix}H$ = +ve, $\Delta_{mix}V$ = +ve
$A - B$ interactions < $A - A$ and $B - B$ interactions.
Negative deviations – Vapour pressure of such solutions shows lower value than expected.
$\Delta_{mix}H$ = –ve, $\Delta_{mix}V$ = –ve
$A - B$ interactions > $A - A$ and $B - B$ interactions.

21. (i) When chloroform is mixed with acetone, it shows negative deviation from ideal behaviour.
(ii) ΔH_{mixing} = +ve, ΔV_{mixing} = +ve
(iii) (a) Nature of liquid (intermolecular force).
(b) Temperature.

OR

A mixture of chloroform and acetone shows negative deviation from Raoult's Law. When these are mixed, the hydrogen bonding takes place between the two molecular species due to which the escaping tendency of the liquid molecules becomes less. Consequently, the vapour pressure decreases resulting in negative deviation from Raoult's law.



22. (i) When the solute molecules undergo dissociation in the solution then the value of van't Hoff's factor is more than 1.
(ii) Here, W_A = 90 g, W_B = 10 g
M_B = 72 + 12 + 96 = 180 g
p_A° = 32.8 mm of Hg, M_A = 18 g

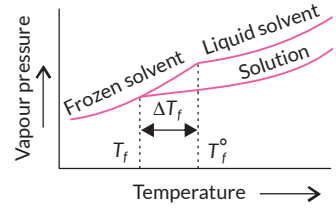
$$M_B = \frac{W_B M_A}{W_A} \times \frac{p_A^\circ}{p_A^\circ - p_S}$$

$$180 = \frac{10 \times 18}{90} \times \frac{32.8}{32.8 - p_S}$$

or $32.8 - p_S = \frac{10 \times 18 \times 32.8}{90 \times 180} = 0.36$

p_S = 32.8 – 0.36 = 32.44 mm of Hg

(iii) **Depression of freezing point :** Addition of non-volatile solute to a solvent decreases its vapour pressure and also its freezing point. This is called depression of freezing point.



23. W_2 = 0.6 g, W_{sol} = 100 g, V = 0.1 L, T = 298 K
W_1 = 100 – 0.6 = 99.4 g, M_2 = 60 g mol^{-1}
$\pi V = nRT$

$$\pi \times 0.1 = \frac{W_2}{M_2} \times RT; \quad \pi \times 0.1 = \frac{0.6}{60} \times 0.0821 \times 298$$

$$\pi = \frac{0.6 \times 0.0821 \times 298}{60 \times 0.1} = 2.446 \text{ atm}$$

Again, p_A° = 24 mm of Hg, p_S = ?

$$\Rightarrow \frac{p_A^\circ - p_S}{p_A^\circ} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1} + \frac{W_2}{M_2}} \Rightarrow 1 - \frac{p_S}{p_A^\circ} = \frac{\frac{0.6}{60}}{\frac{0.6}{60} + \frac{99.4}{18}}$$

$$\Rightarrow 1 - \frac{p_S}{24} = \frac{0.01}{0.01 + 5.52} \Rightarrow 1 - \frac{p_S}{24} = \frac{0.01}{5.53} \Rightarrow \frac{p_S}{24} = 1 - \frac{0.01}{5.53}$$

$$\Rightarrow \frac{p_S}{24} = \frac{5.53 - 0.01}{5.53} \Rightarrow \frac{p_S}{24} = \frac{5.52}{5.53} \Rightarrow p_S = \frac{24 \times 5.52}{5.53}$$

$\therefore$ p_S = 23.957 mm of Hg

24. 20% (*w*/*W*) solution of glucose means that 20 g of glucose is present in 100 g of solution or in 80 g of water.

(i) $\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$

$\text{Moles of glucose} = \frac{20}{180} = 0.1111$

Mass of solvent (water) = 80 g

$\therefore \quad \text{Molality} = \frac{0.1111}{80} \times 1000 = 1.388\,\text{m}$

(ii) $\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in mL)}} \times 1000$

Moles of glucose = 0.1111

$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.20} = 83.3\,\text{mL}$

$\therefore \quad \text{Molarity} = \frac{0.1111}{83.3} \times 1000 = 1.333\,\text{M}$

(iii) Moles of glucose = 0.1111

$\text{Moles of water} = \frac{80}{18} = 4.44$

Total moles = 4.44 + 0.1111 = 4.55

$\text{Mole fraction of glucose} = \frac{0.1111}{4.55} = 0.024$

$\text{Mole fraction of water} = \frac{4.44}{4.55} = 0.976$

25. (i) No. of moles of H_2S = 0.195

No. of moles of $H_2O = \frac{1000}{18} = 55.55$

Mole fraction of $H_2S = \frac{0.195}{0.195 + 55.55} = 0.0035$

Pressure at NTP = 1 atm

According to Henry's law, $p = K_H \cdot x$

or $K_H = \frac{p_{H_2S}}{x_{H_2S}} = \frac{1}{0.0035} = 28.57$ atm

(ii) The liquid pair for which *A*–*B* interactions are stronger than *A*–*A* and *B*–*B* attractive forces, the vapour pressure is less than that for ideal solutions. So, they show negative deviations from Raoult's law. *e.g.*, acetone-chloroform solution.

(iii) Minimum boiling azeotropes : A mixture of liquids which boils at a temperature lower than the boiling temperature of both the components in pure state *e.g.*, ethanol and water.

OR

(i) Reverse osmosis is used for desalination of saline water.

(ii) Both the solutions 4% NaOH (*w*/*V*) and 6% urea (*w*/*V*) have same concentration (1 M) but these are not isotonic because NaOH undergoes dissociation in solution. Therefore, number of particles in NaOH solution is more than that in urea solution.

(iii) Osmotic pressure.

(iv) (a) RBCs are hypertonic with 1% NaCl hence it will shrink due to plasmolysis.

(b) RBCs are hypotonic with pure water hence it will swell or even burst due to endosmosis.

CHAPTER

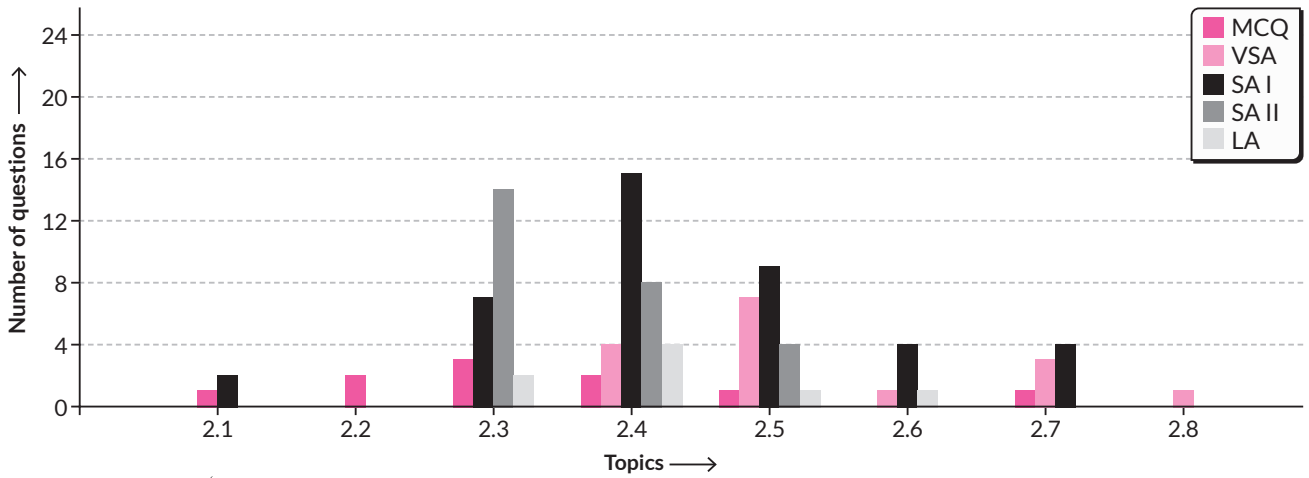
2

Electrochemistry

TOPICS

2.1 Electrochemical Cells
2.2 Galvanic Cells
2.3 Nernst Equation
2.4 Conductance of Electrolytic Solutions
2.5 Electrolytic Cells and Electrolysis
2.6 Batteries
2.7 Fuel Cells
2.8 Corrosion

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topics 2.3 *Nernst Equation* and 2.4 *Conductance of Electrolytic Solutions* are highly scoring topics.
- Maximum VSA, SA I type questions were asked from Topics 2.3, 2.4 and 2.5 *Nernst Equation*, *Conductance of Electrolytic Solutions* and *Electrolytic Cells and Electrolysis*.
- Maximum SA II and LA type questions were asked from Topic 2.3 *Nernst Equation*.

QUICK RECAP

Electrochemistry : It is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

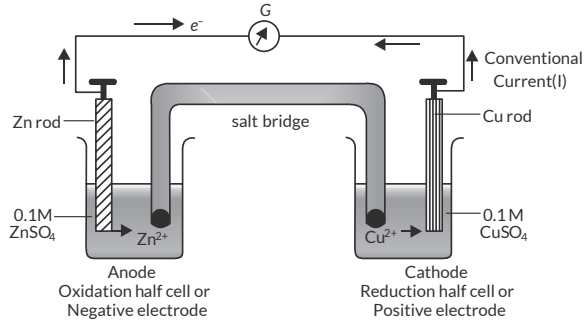
Differences between electrochemical cell and electrolytic cell

Electrolytic cell	Electrochemical cell (Galvanic or Voltaic cell)
1. It is a device which converts electrical energy into chemical energy.	1. It is a device which converts chemical energy into electrical energy.
2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. *i.e.*, ΔG = +ve	2. It is based upon the redox reaction which is spontaneous. *i.e.*, ΔG = –ve
3. Both the electrodes are suspended in the solution or melt of the electrolyte in the same beaker.	3. Two electrodes are usually set up in two separate beakers.
4. Only one electrolyte is taken.	4. The electrolytes taken in the two beakers are different.

5. The electrodes taken may be of the same or different materials.	5. The electrodes taken are of different materials.
6. The electrode which is connected to the –ve terminal of the battery is called the *cathode*; the cations migrate to it which gain electrons and hence, a reduction takes place, the other electrode is called the *anode*.	6. The electrode on which oxidation takes place is called the *anode* (or –ve pole) and the electrode on which reduction takes place is called the *cathode* (or +ve pole)
7. No salt bridge is used in this case.	7. To set up this cell, a salt bridge/porous pot is used.

Reaction in a Galvanic cell :

$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$



Salt bridge : It is U-shaped glass tube filled with a jelly like substance, agar-agar, mixed with an electrolyte like KCl, KNO_3, NH_4NO_3, etc. It performs the following functions :

- It prevents voltage drops, *i.e.*, prevents junction potential.
- It allows flow of current by completing the circuit.
- It prevents accumulation of charges and maintains the electrical neutrality of solutions by intermigration of ions into two half cell reactions.

Characteristics of electrolyte used as salt bridge :

- The electrolyte should be inert and should not react chemically with the electrolyte of either of the two half cells.
- The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, *viz.* KCl, KNO_3, NH_4NO_3, etc.

Representation of a Galvanic cell :

- The interface across which a potential difference exist is shown by single vertical line. *e.g.*,

  $Zn \mid Zn^{2+}$ or $Cu^{2+} \mid Cu$

- When the two solutions are separated by salt bridge, then it is indicated by double vertical line (||), *e.g.*,

  $Cu^{2+} \,||\, Zn^{2+}$

- The oxidation half cell is always written on the left hand side and *vice-versa*. *e.g.*

  $Zn \mid Zn^{2+} \,||\, Cu^{2+} \mid Cu$

- The concentration of the solution, pressure of gases and physical states involved are also indicated in the cell information as :

  $Pt, H_2(0.9\ atm) \mid H^+ (a = 0.1) \,||\, Cu^{2+} (a = 0.1) \mid Cu$

Nernst equation : For a reduction reaction, $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$;

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}_{(aq)}]}$$

At 298 K,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}_{(aq)}]}$$

- For concentration cell, EMF at 298 K is given by

  $$E_{cell} = \frac{0.0591}{n}\log\frac{C_2}{C_1} \quad \text{where } A^{2+}(C_2) \longrightarrow A^{2+}(C_1)$$

  When electrolytic solution present in both beakers are same then,

  $E^\circ_{cell} = 0$

Applications of Nernst equation :

- **To calculate electrode potential of a cell :**

  $$aA + bB \xrightarrow{ne^-} xX + yY$$

  $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b} \text{ (At 298 K)}$$

- **To calculate equilibrium constant :**

  At equilibrium, $E_{cell} = 0$

  $$E^\circ_{cell} = \frac{0.0591}{n}\log K_c \text{ at 298 K}$$

Types of Substances on the Basis of Conductivity

Materials are classified into following types :

Insulators : Substances which have very low conductivity in the range of 10^{-20} to 10^{-10} S m^{-1} are called insulators *e.g.*, plastics, wood, coal, etc.

Semiconductors : Substances which have moderate conductivity in the range of 10^{-6} to 10^4 S m^{-1} are called semiconductors. These are intrinsic and extrinsic semiconductors.

Conductors : Substances which have very large conductivity in the range of 10^4 to 10^7 S m^{-1} are known as conductors *e.g.*, metals and their alloys. Certain non-metals like carbon black, graphite and some organic polymers.

Superconductors : Materials which have zero resistivity and infinite conductivity are called superconductors *e.g.*, metals and their alloys at very low temperature 0 to 15 K. Ceramic materials and mixed oxides behave as superconductors upto 150 K.

TYPES OF CONDUCTANCE

Metallic or electronic conductance : Electrical conductance through metals due to movement of

electrons is called electronic or metallic conductance *e.g.*, all metals, alloys, graphite and conducting polymers.

Factors affecting electronic conductance :

- The nature and structure of the metal.
- The number of valence electrons per atom.
- Temperature (electronic conductance decreases with increasing temperature.)

Electrolytic or ionic conductance : The conductance of electricity by ions present in the solution or melt is called ionic or electrolytic conductance. In ionic conductance, ions carry charge from one electrode to another.

Factors affecting ionic conductance :

- The nature of the electrolyte added.
- Size of the ions produced.
- The nature and viscosity of solvent.
- Solvation of the ions.
- Concentration of electrolyte.
- Temperature (electrolytic conductivity increases with increasing temperature because speed of ions increases).

MEASUREMENT OF CONDUCTIVITY OF IONIC SOLUTIONS

Conductance of an ionic solution is measured by measuring its resistance with the help of Wheatstone bridge.

First of all, cell constant of the conductivity cell is measured by measuring the resistance of solution whose conductivity is already known. The cell constant is calculated using formula $G^* = \frac{l}{A} = \kappa \cdot R$

- Conductivity of the solution is calculated by using formula,

$$\kappa = \frac{G^*}{R} = \frac{\text{Cell constant}}{\text{Resistance}}$$

- Molar conductance Λ_m is calculated by using formula $\Lambda_m = \frac{\kappa}{M}$ where, M is molarity of solution.

Relation between cell potential and Gibbs energy change :

$\Delta G^\circ = -nFE^\circ_{cell}$; $\Delta G^\circ = -2.303\, RT \log K_c$

Conductance in electrolytic solutions :

Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{A}{\rho l} = \frac{\kappa A}{l}$	Ohm^{-1} (Ω^{-1}) or Siemens (S)	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G\frac{l}{A}$	$Ohm^{-1}\,cm^{-1}$ or $S\,m^{-1}$	Decreases as number of ions per cm^3 decreases.
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	$\Omega^{-1}\,cm^2\,mol^{-1}$ or $S\,m^2\,mol^{-1}$	Increases with dilution due to large increase in V.

Limiting molar conductivity : When concentration of electrolyte approaches zero *i.e.*, at infinite dilution, the molar conductivity is known as *limiting molar conductivity* (Λ°_m).

Variation of molar conductivity with concentration : For a strong electrolyte it is shown by *Debye-Huckel Onsager equation* as follows :

$$\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$$

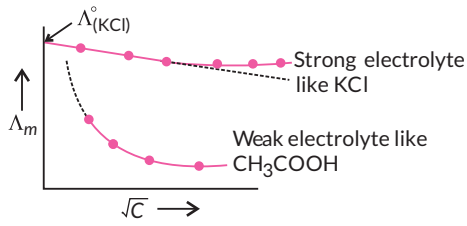
Here, Λ°_m = Molar conductivity at infinite dilution (Limiting molar conductivity)

Λ_m = Molar conductivity at V-dilution

A = Constant which depends upon nature of solvent and temperature

C = Concentration

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ°_m and slope equal to '$-A$'.



Thus, Λ_m decreases linearly with $\sqrt{C}$, when C = 0, $\Lambda_m = \Lambda^\circ_m$ and Λ°_m can be determined experimentally.

- **For weak electrolytes :** There is a very large increase in conductance with dilution especially near infinite dilution as no. of ions increases. Λ_m increases as C decreases but does not reach a constant value even at infinite dilution. Hence, their Λ°_m cannot be determined experimentally.
- **For strong electrolytes :** There is only a small increase in conductance with dilution. This is because a strong electrolyte is completely dissociated in solution and so, the number of ions remain constant and on dilution, interionic attractions decreases as ions move far apart.

Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. $\Lambda^\circ_m = \upsilon_+\lambda^\circ_+ + \upsilon_-\lambda^\circ_-$; where λ°_+ and λ°_- are the limiting molar conductivities of the cation and anion respectively and υ_+ and υ_- are stoichiometric number of cations and anions respectively in one formula unit of the electrolyte.

Applications of Kohlrausch's law :

- **Calculation of molar conductivity of weak electrolytes :**

$$\Lambda^\circ_{m\,(CH_3COOH)} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

$$= \left(\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}\right) + \left(\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}\right) - \left(\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}\right)$$

$$= \Lambda^\circ_{m\,(HCl)} + \Lambda^\circ_{m\,(CH_3COONa)} - \Lambda^\circ_{m\,(NaCl)}$$

- **Calculation of degree of dissociation :**

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m}{\Lambda^\circ_m}$$

$$= \frac{\text{Molar conductivity at concentration 'c'}}{\text{Molar conductivity at infinite dilution}}$$

- **Calculation of dissociation constant (K_c) of weak electrolyte :**

	AB	$\rightleftharpoons$	A^+	$+$	B^-
Initial conc.	c		0		0
Conc. at eqm.	$(c - c\alpha)$		$c\alpha$		$c\alpha$

$$K_c = \frac{c\alpha \times c\alpha}{(c - c\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

Electrolysis : It is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.

- **Faraday's first law of electrolysis :** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).
  $w \propto Q$ or $w = ZQ = Z \times I \times t$; where, Z is electrochemical equivalent of the substance deposited and $Z = \frac{\text{Eq. wt. of substance}}{96500}$.
- **Faraday's second law of electrolysis :** The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

$\frac{w_1}{w_2} = \frac{E_1}{E_2}$ where E is the equivalent weight.

Equivalent weight

$$= \frac{\text{Atomic mass of metal}}{\text{No. of electron required to reduce the cation}}$$

Products of electrolysis :

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl_2 gas	$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$	$Cl^-_{(l)} \rightarrow \frac{1}{2} Cl_{2(g)} + e^-$
Aqueous NaCl	H_2 gas	Cl_2 gas	$H_2O_{(l)} + e^- \rightarrow \frac{1}{2} H_{2(g)} + OH^-_{(aq)}$	$Cl^-_{(aq)} \rightarrow \frac{1}{2} Cl_{2(g)} + e^-$
Dil. H_2SO_4	H_2 gas	O_2 gas	$H^+_{(aq)} + e^- \rightarrow \frac{1}{2} H_{2(g)}$	$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
Conc. H_2SO_4	H_2 gas	$S_2O_8^{2-}$	$H^+_{(aq)} + e^- \rightarrow \frac{1}{2} H_{2(g)}$	$2SO^{2-}_{4(aq)} \rightarrow S_2O^{2-}_{8(aq)} + 2e^-$

Batteries

Combination of one or more than one cell in series

Primary Cell
Cells once exhausted cannot be used again *e.g.*, Dry cell used in transistor and clocks.
Mercury cell suitable for low current devices like hearing aids, watches etc.

Secondary Cell
Rechargeable cell which can be used again and again *e.g.*, Nickel cadmium cell
Lead storage battery used in automobiles and inverters.

- **Fuel cells :** Cells which can convert the energy of combustion of fossil fuels (coal, gas or oil) directly into electrical energy are known as fuel cells, *e.g.*, $H_2 - O_2$ fuel cell. In fuel cells, combustion reaction is also considered as redox reaction.

  Anode $\rightarrow$ Porous carbon containing suitable catalyst

  Cathode $\rightarrow$ Porous carbon containing suitable catalyst

  Electrolyte $\rightarrow$ Concentrated aqueous KOH NaOH

  Reaction :

  At anode : $2H_{2(g)} + 4OH^-_{(aq.)} \rightarrow 4H_2O_{(l)} + 4e^-$

  At cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq.)}$

  Overall reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

Dry cell, lead accumulator and fuel cell :

	Dry cell	Lead storage battery	Fuel cell
Anode	Zinc	Lead	Porous carbon and Pt/Pd containing catalysts (H_2 passed)
Cathode	Graphite	Lead dioxide	Porous carbon and Pt/Pd containing catalysts (O_2 passed)
Electrolyte	MnO_2 + C (touching cathode) $NH_4Cl + ZnCl_2$ (touching anode)	H_2SO_4 (38%)	Conc. aqueous KOH
Anode reaction	$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$	$Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$	$H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^-$
Cathode reaction	$MnO_{2(s)} + NH^+_{4(aq)} + e^- \rightarrow MnO(OH)_{(s)} + NH_{3(g)}$	$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+ + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Corrosion : The slow eating away of metals when exposed to the atmosphere is called *corrosion*.

Corrosion of iron (rusting) : It is an electrochemical phenomenon which occurs in the presence of moisture and oxygen.

At anode : $2Fe_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + 4e^-$

At cathode : $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$

Overall reaction : $2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)}$.

Methods used for prevention of corrosion : Barrier protection, sacrificial protection, antirust solutions.

Hydrogen Economy

- Hydrogen can be used as renewable and non-polluting source of energy. Water will split to hydrogen and oxygen using solar energy.

$$H_2O_{(l)} \xrightarrow{h\upsilon} H_{2(g)} + \frac{1}{2}O_{2(g)}$$

Combustion of hydrogen in a fuel cell will produce water.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

- Both these technologies are based on electrochemical principles. This production of energy will be very economical in comparison to fossil fuels and nuclear energy.

ELECTROCHEMISTRY

It is the branch of chemistry which deals with the study of relationship between electrical and chemical changes taking place in a redox reaction.

Basic Terms Used

Conductance (C) : $C = \frac{1}{R}$

Conductivity (κ) : $\kappa = \frac{1}{\rho} = \frac{l}{RA}$

Equivalent Conductivity (Λ_{eq}) :

$$\Lambda_{eq} = \frac{\kappa}{C} \times 1000$$

where

κ = specific conductance

C = Concentration in g. equivalent

Molar Conductivity (Λ_m) :

$$\Lambda_m = \frac{\kappa}{C} \times 1000$$

where

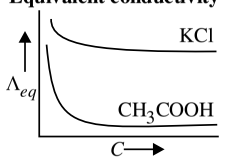
κ = specific conductance

C = molar concentration

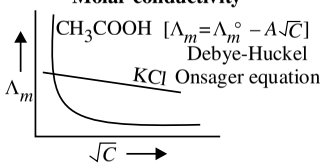
Variation of Conductivity with Concentration

Conductivity

Equivalent conductivity



Molar conductivity



Nernst Equation

Nernst Equation and Electrochemical Series

- **Nernst equation :** For the reaction : $M^{n+} + ne^- \rightarrow M$,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{M}{[M^{n+}]} \text{ or}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \text{ at 298 K}$$

- **For concentration cell :**

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1};$$

E_{cell} = +ve if $C_2 > C_1$

At equilibrium

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_c \text{ at 298 K}$$

- **Electrochemical series :** It is the arrangement of electrodes in order of increasing standard reduction potentials.
  - This series helps in comparing the relative oxidizing or reducing powers, relative activities of metals and to predict spontaneity of the redox reaction.

Types of Cells

Electrolytic Cells: These are the cells in which electricity is passed through the solution of an electrolyte so as to bring about redox reaction.

Electrochemical Cells : These are the cells in which electrical energy is produced by virtue of redox reactions.

Type	Energy change	Anode	Cathode
Electrolytic cell	Electrolytic energy → Chemical energy	+	–
Galvanic (Voltaic cell)	Chemical energy → Electrical energy	–	+

Dry Cells

Anode : $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode : $2NH^+_{4(aq)} + 2MnO_{2(s)} + 2e^- \rightarrow 2MnO(OH) + 2NH_3$

Net reaction : $Zn_{(s)} + 2NH^+_{4(aq)} + 2MnO_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2MnO(OH) + 2NH_3$

Lead Storage Cells

Cell reaction during use of battery :

Anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

Cathode : $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

$H_2 - O_2$ Fuel Cell

Anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Net reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

Laws

- **Faraday's first law :** $W = ZIt$
- **Faraday's second law :**

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

- **Kohlrausch law :** For an electrolyte A_xB_y,

$$\Lambda^\circ_m = x\lambda^\circ_+ + y\lambda^\circ_-$$

or $\Lambda^\circ_{eq} = \lambda^\circ_+ + \lambda^\circ_-$

Potentials

Electrode Potential : It is defined as the tendency of an electrode to either lose or gain of electrons *i.e.*, tendency to get either oxidised or reduced when it is in contact with a solution of its own ions is known as electrode potential.

Cell Potential : The difference between electrode potentials of two half cells is called cell potential or cell voltage or electromotive force (EMF) of the cell.

BRAIN MAP

Previous Years' CBSE Board Questions

2.1 Electrochemical Cells

MCQ

1. An electrochemical cell behaves like an electrolytic cell when
   (a) $E_{cell} = E_{external}$ (b) $E_{cell} = 0$
   (c) $E_{external} > E_{cell}$ (d) $E_{external} < E_{cell}$
   (2020) R

SA I (2 marks)

2. Give two points of differences between electrochemical and electrolytic cells.
   (2/5, 2020) R
3. Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell?
   (AI 2019, 2/5, AI 2016) U

2.2 Galvanic Cells

MCQ

4. The correct cell to represent the following reaction is
   $$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$$
   (a) $2Ag \mid Ag^+ \mid\mid Zn \mid Zn^{2+}$ (b) $Ag^+ \mid Ag \mid\mid Zn^{2+} \mid Zn$
   (c) $Ag \mid Ag^+ \mid\mid Zn \mid Zn^{2+}$ (d) $Zn \mid Zn^{2+} \mid\mid Ag^+ \mid Ag$
   (2023)
5. If the standard electrode potential of an electrode is greater than zero, then we can infer that its
   (a) reduced form is more stable compared to hydrogen gas
   (b) oxidised form is more stable compared to hydrogen gas
   (c) reduced and oxidised forms are equally stable.
   (d) reduced form is less stable than the hydrogen gas. *(2020)* U

2.3 Nernst Equation

MCQ

6. ΔG and E°_{cell} for a spontaneous reaction will be
   (a) positive, negative (b) negative, negative
   (c) negative, positive (d) positive, positive.
   (2023)
7. $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$; $E^\circ = +0.80$ V
   $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$; $E^\circ = -0.44$ V
   Find the E°_{cell} for :
   $Fe_{(s)} + 2Ag^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)}$
   (a) 1.6 V (b) −1.16 V (c) 2.04 V (d) 1.24 V
   (2023)
8. Consider the following standard electrode potential values
   $Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E^\circ = -0.14$ V
   $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ $E^\circ = +0.77$ V
   What is the cell reaction and potential for the spontaneous reaction that occurs?
   (a) $2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + Sn_{(s)}$; $E^\circ = -0.91$ V
   (b) $2Fe^{3+}_{(aq)} + Sn_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$; $E^\circ = +0.91$ V
   (c) $2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + Sn_{(s)}$; $E^\circ = +0.91$ V
   (d) $2Fe^{3+}_{(aq)} + Sn_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$; $E^\circ = +1.68$ V
   (2023)

SA I (2 marks)

9. Calculate the emf of the following cell at 298 K:
   $Fe_{(s)} \mid Fe^{2+}(0.01\ M) \mid\mid H^+_{(1M)} \mid H_{2(g)}$ (1 bar), $Pt_{(s)}$
   Given $E^\circ_{cell} = 0.44$ V. *(2023)*
10. Calculate $\Delta_r G^\circ$ for the cell reaction at 25°C:
    $Zn \mid Zn^{2+} \mid\mid Cd^{2+} \mid Cd$
    Given that : $E^\circ_{Zn^{2+}/Zn} = -0.76$ V,
    $E^\circ_{Cd^{2+}/Cd} = 0/.40$ V, 1 F = 96500 C mol^{-1} *(2023)*
11. Write the Nernst equation for the following cell reaction:
    $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
    How will the E_{cell} be affected when concentration of
    (i) Cu^{2+} ions is increased and
    (ii) Zn^{2+} ions is increased? *(Term II, 2021-22)*
12. For an electrochemical cell
    $Mg_{(s)} + Ag^+_{(aq)} \longrightarrow Ag_{(s)} + Mg^{2+}_{(aq)}$,
    give the cell representation. Also write the Nernst equation for the above cell at 25°C. *(2020)*
13. Calculate the emf of the following cell at 25°C :
    $Al_{(s)} \mid Al^{3+}(0{\cdot}001\ M) \mid\mid Ni^{2+}(0.1\ M) \mid Ni_{(s)}$
    Given : $E^\circ_{(Ni^{2+}/Ni)} = -0{\cdot}25$ V
    $E^\circ_{(Al^{3+}/Al)} = -1{\cdot}66$ V
    [log 2 = 0·3010, log 3 = 0·4771] *(2019)* Ev
14. Calculate $\Delta_r G^\circ$ for the reaction :
    $Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$
    Given $E^\circ_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1}
    (2/3,AI 2014) Ap
15. Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E°_{cell}.
    $A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$ *(2/3,Foreign 2014)*

SA II (3 marks)

16. Write the Nernst equation and calculate the emf of the following cell at 298 K :

$Zn \mid Zn^{2+}$ (0.001 M) || H^+ (0.01 M) | $H_{2(g)}$ (1 bar) | $Pt_{(s)}$
Given : $E^\circ_{Zn^{2+}/Zn} = -0.76$ V, $E^\circ_{H^+/H_2} = 0.00$ V, [log 10 = 1]
(Term II, 2021-22, Foreign 2015) Cr

17. Calculate $\Delta_r G^\circ$ and log K_c for the following cell :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$
Given that $E^\circ_{cell} = 1.05$ V, 1F = 96,500 C mol^{-1}
(Term II, 2021-22)

OR

Calculate the maximum work and logK_c for the given reaction at 298 K :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Ni^{2+}_{(aq)} + 2Ag_{(s)}$
Given : $E^\circ_{Ni^{2+}/Ni} = -0.25$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V
1F = 96500 C mol^{-1} *(2020)*

OR

For the cell reaction,
$Ni_{(s)} |Ni^{2+}_{(aq)}||Ag^+_{(aq)}|Ag_{(s)}$
Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by operation of this cell?
$E^\circ_{(Ni^{2+}/Ni)} = -0.25$ V and $E^\circ_{Ag^+/Ag} = 0.80$V
(3/5, Delhi 2015C)

18. Calculate the e.m.f. of the following cell at 298K :
$Fe_{(s)} \mid Fe^{2+}$ (0.001 M) | | H^+ (0.01 M) | $H_{2(g)}$ (1 bar) | $Pt_{(s)}$
Given that $E^\circ_{cell} = +0.44$ V
[log 2 = 0.3010, log 3 = 0.4771, log 10 = 1]
(Term II, 2021-22) Ev

OR

Calculate emf of the following cell at 25°C:
$Fe|Fe^{2+}(0.001\ M)||H^+(0.01\ M)|H_{2(g)}(1\ bar)|Pt_{(s)}$
$E^\circ_{(Fe^{2+}/Fe)} = -0.44$ V, $E^\circ_{(H^+/H_2)} = 0.00$ V *(Delhi 2015)*

19. Calculate ΔG° for the reaction,
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
Given : E° for $Zn^{2+}/Zn = -0.76$ V and
E° for $Cu^{2+}/Cu = +0.34$ V
$R = 8.314$ J K^{-1} mol^{-1}, 1 $F = 96500$ C mol^{-1}.
(3/5, 2020)

20. Calculate e.m.f of the following cell :
$Zn_{(s)} \mid Zn^{2+}$ (0.1 M) || Ag^+ (0.01 M) | $Ag_{(s)}$
Given : $E^\circ_{Zn^{2+}/Zn} = -0.76$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V
[Given : log 10 = 1] *(3/5, 2020)*

21. Calculate $\Delta_r G^\circ$ and log K_c for the following reaction.
$Cd^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + Cd_{(s)}$
Given : $E^\circ_{Cd^{2+}/Cd} = -0.403$ V ; $E^\circ_{Zn^{2+}/Zn} = -0.763$ V
(AI 2019) Ap

22. Zinc rod is dipped in 0·01 M solution of zinc sulphate when temperature is 298 K. Calculate the electrode potential of zinc.
(Given : $E^\circ_{Zn^{2+}/Zn}$ = = −0·76 V; log 10 = 1) *(2019C)* Ev

23. Write the cell reaction and calculate the e.m.f. of the following cell at 298 K.
$Sn_{(s)} \mid Sn^{2+}$ (0.004 M) || H^+(0.020 M) | $H_{2(g)}$ (1 bar) | $Pt_{(s)}$
(Given : $E^\circ_{Sn^{2+}/Sn} = -0.14$ V) *(3/5, 2018)* U

24. For the reaction,
$2AgCl_{(s)} + H_{2(g)}$ (1 atm) $\rightarrow 2Ag_{(s)} + 2H^+$(0.1 M) + $2Cl^-$(0.1 M)
$\Delta G^\circ = -43600$ J at 25 °C.
Calculate the e.m.f. of the cell. (log $10^{-n} = -n$)
(3/5, 2018)

25. Calculate e.m.f. of the following cell at 298 K.
$2Cr_{(s)} + 3Fe^{2+}(0.1M) \rightarrow 2Cr^{3+}(0.01M) + 3Fe_{(s)}$
Given : $E^\circ_{(Cr^{3+}/Cr)} = -0.74$ V, $E^\circ_{(Fe^{2+}/Fe)} = -0.44$ V
(Delhi 2016)

26. Calculate E°_{cell} for the following reaction at 298 K.
$2Al_{(s)} + 3Cu^{2+}(0.01M) \rightarrow 2Al^{3+}(0.01M) + 3Cu_{(s)}$
Given : $E_{cell} = 1.98$ V *(3/5,AI 2016)*

27. Calculate the standard cell potential of the galvanic cell in which the following reaction takes place :
$Fe^{2+}_{(aq)} + Ag^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ag_{(s)}$
Calculate the $\Delta_r G^\circ$ and equilibrium constant of the reaction.
$\left(E^\circ_{Ag^+/Ag} = 0.80\,V ; E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\,V\right)$
(3/5, Delhi 2015C) U

28. Calculate the emf of following cell at 298 K :
$Mg_{(s)} \mid Mg^{2+}$(0.1 M) || Cu^{2+}(0.01 M)|$Cu_{(s)}$
[Given : $E^\circ_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1}]
(3/5, Delhi 2014)

29. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The Gibbs energy change for the decomposition reaction,
$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$ is 960 kJ. ($F = 96500$ C mol^{-1})
(3/5,Delhi 2014C)

LA (5 marks)

30. E°_{cell} for the given redox reaction is 2.71 V.
$Mg_{(s)} + Cu^{2+}(0.01M) \rightarrow Mg^{2+}(0.001M) + Cu_{(s)}$
Calculate E_{cell} for the reaction. Write the direction of flow of current when an external opposite potential applied is
(i) less than 2.71 V and
(ii) greater than 2.71 V *(Delhi 2019)*

31. Calculate e.m.f and ΔG for the following cell
$Mg_{(s)} \mid Mg^{2+}$ (0.001 M) || Cu^{2+} (0.0001 M) | $Cu_{(s)}$
$E^\circ_{(Mg^{2+}/Mg)} = -2{\cdot}37$ V, $E^\circ_{(Cu^{2+}/Cu)} = +0.34$ V
(NCERT, AI 2015)

2.4 Conductance of Electrolytic Solutions

MCQ

32. The unit of molar conductivity is
(a) S cm^{-2} mol^{-1} (b) S cm^2 mol^{-1}
(c) S^{-1} cm^2 mol^{-1} (d) S cm^2 mol *(2023)*

33. **Assertion (A) :** Conductivity of an electrolyte increases with decrease in concentration.
Reason (R) : Number of ions per unit volume decreases on dilution.

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is wrong statement.
(d) Assertion (A) is wrong, but Reason (R) is correct statement. *(2020)* An

VSA (1 mark)

34. Give reason :
Conductivity of CH_3COOH decreases on dilution. *(1/5, 2018)* U

35. Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration? *(1/2, Delhi 2015)*

OR

Define the following term :
Limiting molar conductivity *(1/5, Delhi 2014)*

36. State Kohlrausch's law of independent migration of ions. Write its one application. *(1/2, Foreign 2015)*

OR

Define the following term :
Kohlrausch's law of independent migration of ions. *(1/5, Delhi 2015C)* R

37. Define the following term :
Molar conductivity (Λ_m) *(1/5, Delhi 2015C)*

SA I (2 marks)

38. On diluting two electrolytes '*A*' and '*B*', then Λ_m of '*A*' increases 25 times while that of '*B*' increases by 1.5 times. Which of the two electrolytes is strong? Justify your answer graphically. *(2023)*

39. (i) State Kohlrausch's law of independent migration of ions.
(ii) Calculate the degree of dissociation (α) of CH_3COOH if Λ_m and Λ°_m of CH_3COOH are 48 S cm^2 mol^{-1} and 400 S cm^2 mol^{-1} respectively. *(Term II, 2021-22)*

40. The conductivity of 0.001 M acetic acid is 7.8×10^{-5} S cm^{-1}. Calculate its degree of dissociation if Λ°_m for acetic acid is 390 S cm^2 mol^{-1}. *(Term II, 2021-22)* Ap

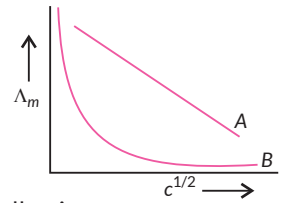
41. In a plot of Λ_m against the square root of concentration ($C^{1/2}$) for strong and weak electrolyte, the value of limiting molar conductivity of a weak electrolyte cannot be obtained graphically. Suggest a way to obtain this value. Also state the related law, if any. *(Term II, 2021-22)* EV

42. Answer the following questions (Any two) :
(a) Define molar conductivity (Λ_m).
(b) Write the unit of Λ_m.
(c) How does Λ_m vary with concentration? *(Term II,2021-22 C)*

43. Answer the following questions (Any two) :
(a) Why is alternating current used instead of direct current for measuring resistance of an electrolytic solution ?
(b) State Kohlrausch's law of independent migration of ion.
(c) Depict the Galvanic cell in which the following reaction takes place :
$Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$ *(Term II, 2021-22C)*

44. *X* and *Y* are two electrolytes. On dilution molar conductivity of '*X*' increases 2.5 times while that *Y* increases 25 times. Which of the two is a weak electrolyte and why? *(2/5, 2020)* Ap

45. In the plot of molar conductivity (Λ_m) *vs* square root of concentration ($c^{1/2}$),following curves are obtained for two electrolytes *A* and *B*



Answer the following :
(i) Predict the nature of electrolytes *A* and *B*.
(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes *A* and *B*? *(2/5, Delhi 2019)* Ev

46. Explain with a graph, the variation of molar conductivity of a strong electrolyte with dilution. *(2019)*

47. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.
(Given : $\lambda°(H^+)$ = 349.68 S $cm^2 mol^{-1}$ and $\lambda°(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1}) *(Delhi 2017)*

48. Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation. *(2/5, Delhi 2015C)* Cr

49. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. *(NCERT, 2/5, AI 2015C)*

50. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? *(AI 2014)*

51. Define the terms conductivity and molar conductivity for the solution of an electrolyte. Comment on their variation with temperature. *(Delhi, AI 2014C)* U

52. The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the solution. *(2/3, AI 2014C)*

SA II (3 marks)

53. (a) The standard Gibbs energy ($\Delta_r G°$) for the following cell reaction is -300 kJ mol^{-1} :
$Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$

Calculate E°_{cell} for the reaction.
(Given: 1F = 96500 C mol^{-1})

(b) Calculate λ°_m for $MgCl_2$ if λ° values for Mg^{2+} ion and Cl^- ion are 106 S cm^2 mol^{-1} and 76.3 S cm^2 mol^{-1} respectively. *(Term I, 2021-22)*

54. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}.Calculate its molar conductivity and degree of dissociation (α).
[Given : $\lambda^\circ(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^\circ(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}]
(Term II, 2021-22C, 3/5, AI 2016)

55. Conductivity of 2×10^{-3} M methanoic acid is 8×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation if Λ°_m for methanoic acid is 404 S cm^2 mol^{-1}. *(2020)*

56. Out of the following pairs, predict with reason which pair will allow greater conduction of electricity.
(i) Silver wire at 30°C or silver wire at 60 °C.
(ii) 0.1 M CH_3COOH solution or 1 M CH_3COOH solution.
(iii) KCl solution at 20 °C or KCl solution at 50 °C.
(3/5, 2020)

57. The electrical resistance of a column of 0.05 M KOH solution of length 50 cm and area of cross-section 0.625 cm^2 is 5×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. *(3/5, 2020)*

58. (a) Following reaction takes place in the cell :
$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$
Calculate $\Delta_r G^\circ$ of the reaction..
[Given : $E^\circ_{(Zn^{2+}/Zn)} = -0.76$ V,
$E^\circ_{(Ag^+/Ag)} = 0{\cdot}80$ V, 1 F = 96,500 C mol^{-1}]

(b) How can you determine limiting molar conductivity, (Λ°_m) for strong electrolyte and weak electrolyte ? *(2019)*

59. The conductivity of 0.20 mol L^{-1} solution of KCl is 2.48×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
Given : $\lambda^\circ(K^+) = 73.5$ S cm^2 mol^{-1} and
$\lambda^\circ(Cl^-) = 76.5$ S cm^2 mol^{-1}. *(AI 2015)*

60. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29×10^{-2} Ω^{-1} cm^{-1}.
(3/5, AI 2014) Ap

LA (4/5 marks)

61. Rahul set up an experiment to find resistance of aqueous KCl solution for different concentrations at 298 K using a conductivity cell connected to a Wheatstone bridge. He fed the Wheatstone bridge with a.c. power in the audio frequency range 550 to 5000 cycles per second. Once the resistance was calculated from null point he also calculated the conductivity κ and molar conductivity Λ_m and recorded his readings in tabular form.

S.No.	Conc. (M)	κ (S cm^{-1})	Λ_m (S cm^2 mol^{-1})
1.	1.00	111.3×10^{-3}	111.3
2.	0.10	12.9×10^{-3}	129.0
3.	0.01	1.41×10^{-3}	141.0

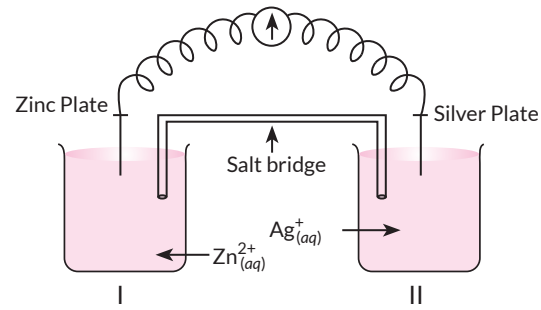
Answer the following questions:

(a) Why does conductivity increase though the conductivity decrease with dilution?

(b) If Λ°_m of KCl is 150.0 S cm^2 mol^{-1}, calculate the degree of dissociation of 0.01 M KCl.

(c) If Rahul had used HCl instead to KCl then would you expect the Λ_m values to be more or less than those per KCl for a given concentration. Justify. *(2023)*

62. **Read the passage given below and answer the questions that follow :**
Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a voltaic/galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E°_{cell} is positive the reaction is spontaneous and if it is negative the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.
The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by *k* and it depends upon nature and concentration of electrolyte, temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.



(a) Is silver plate the anode or cathode ?
(b) What will happen if the salt bridge is removed ?
(c) When does electrochemical cell behave like an electrolytic cell ?
(d) (i) What will happen to the concentration of Zn^{2+} and Ag^{+} when $E_{cell} = 0$.
(ii) Why does conductivity of a solution decreases with dilution ?

OR

(d) The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution.
(Term II, 2021-22)

63. (i) The electrical resistance of a column of 0·02 M NaOH solution of diameter 1·40 cm and length 44 cm is 5·00 x 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.
(ii) Depict the galvanic cell in which the reaction takes place :
$Ni_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$
Further show :
(i) Which of the electrodes is positively charged ?
(ii) The carriers of the current in the outer circuit.
(2021C) An

64. (a) Represent the cell in which the following reaction takes place :
$2Al_{(s)} + 3Ni^{2+}$ (0·1 M) $\rightarrow 2Al^{3+}$ (0·01 M) $+ 3Ni_{(s)}$
Calculate its emf if $E^{\circ}_{cell} = 1{\cdot}41$ V.
(b) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte ? How can you obtain limiting molar conductivity (Λ°_m) for weak electrolyte ? *(2019)*

2.5 Electrolytic Cells and Electrolysis

MCQ

65. Four half reactions I to IV are shown below:
I. $2Cl^{-} \rightarrow Cl_2 + 2e^{-}$
II. $4OH^{-} \rightarrow O_2 + 2H_2O + 2e^{-}$
III. $Na^{+} + e^{-} \rightarrow Na$
IV. $2H^{+} + 2e^{-} \rightarrow H_2$
Which two of these reactions are most likely to occur when concentrated brine is electrolysed?
(a) I and III (b) I and IV
(c) II and III (d) II and IV *(2023)*

VSA (1 mark)

66. How much charge in terms of Faraday is required to reduce one mol of MnO_4^{-} to Mn^{2+}? *(2020)* Ev

67. How many coulombs are required for the oxidation of 1 mol of H_2O to O_2? *(One word, 2020)*

68. Give reason :
On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl. *(1/5, 2018)* U

69. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :
$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$, $E^{\circ} = +0.80$ V
$H^{+}_{(aq)} + e^{-} \rightarrow \frac{1}{2}H_{2(g)}$, $E^{\circ} = 0.00$ V
On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? *(AI 2017C, 1/2, Delhi 2015)*

70. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn? *(Delhi 2015)*

71. Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution :
$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$; $E^{\circ} = +0.34$ V
$H^{+}_{(aq)} + e^{-} \rightarrow \frac{1}{2}H_{2(g)}$; $E^{\circ} = 0.00$ V
On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? *(1/2, Foreign 2015)* Ev

72. State the Faraday's first law of electrolysis.
(Delhi 2015C) R

SA I (2 marks)

73. (i) What should be the signs (positive/negative) for E°_{cell} and ΔG° for a spontaneous redox reaction occurring under standard conditions?
(ii) State Faraday's first law of electrolysis. *(2023)*

74. Predict the products of electrolysis of an aqueous solution of $CuCl_2$ with platinum electrodes.
(Given : $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V,
$E^{\circ}_{(1/2Cl_2/Cl^{-})} = +1.36$ V
$E^{\circ}_{H^{+}/H_{2(g)}, Pt} = 0.00$ V, $E^{\circ}_{(1/2O_2/H_2O)} = +1.23$ V)
(2/5, 2020)

75. Predict the products of electrolysis in each of the following :
(a) An aqueous solution of $CuSO_4$ with Pt electrode
(b) An aqueous solution of $AgNO_3$ with Pt electrode
(2020C)

76. How many seconds does it require to reduce 3 moles of Fe^{3+} to Fe^{2+} with 2 A current?
(Given : 1 F = 96500 C mol^{-1}) *(2020C)*

77. Following reactions may occur at cathode and anode during electrolysis of aqueous sodium chloride. What products will be held at anode and cathode? Use given E° values to justify your answer.
Cathode : $Na^{+}_{(aq)} + e^{-} \rightarrow Na_{(s)}$ $E^{\circ} = -2{\cdot}71$ V
$H^{+}_{(aq)} + e^{-} \rightarrow \frac{1}{2}H_{2(g)}$ $E^{\circ} = 0{\cdot}00$ V
Anode : $Cl^{-}_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^{-}$ $E^{\circ} = +1{\cdot}36$ V
$2H_2O_{(aq)} \rightarrow O_{2(g)} + 4H^{+} + 4e^{-}$ $E^{\circ} = +1{\cdot}23$ V
(2019) Ap

78. Calculate the mass of Ag deposited at cathode when a current of 2 ampere was passed through a solution of $AgNO_3$ for 15 minutes.

(Given : Molar mass of Ag = 108 g mol^{-1}, 1 F = 96500 C mol^{-1}) *(2/3, Delhi 2017)*

79. State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu? *(2/5, Delhi 2014)*

80. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode?
(Given : At. mass of Ni = 58.7 g mol^{-1}, 1F = 96500 C mol^{-1}) *(Foreign 2014)*

81. Predict the products of electrolysis in each of the following :
(i) An aqueous solution of $AgNO_3$ with platinum electrodes.
(ii) An aqueous solution of H_2SO_4 with platinum electrodes. *(2/5, Delhi 2014C)*

SA II (3 marks)

82. When a steady current of 2A was passed through two electrolytic cells *A* and *B* containing electrolytes $ZnSO_4$ and $CuSO_4$ connected in series, 2 g of Cu were deposited at the cathode of cell *B*. How long did the current flow ?
What mass of Zn was deposited at cathode of cell *A*?
[Atomic mass : Cu = 63.5 g mol^{-1}, Zn = 65 g mol^{-1}; 1F = 96500 C mol^{-1}] *(2020)* Ev

83. A steady current of 2 amperes was passed through two electrolytic cells *X* and *Y* connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8 g of Fe deposited at the cathode of cell *X*. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell *Y*. (Molar mass : Fe = 56 g mol^{-1}, Zn = 65.3 g mol^{-1}, 1 F = 96500 C mol^{-1}) *(3/5, Delhi 2019)*

84. Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation :
$CrO_{3(aq)} + 6H^+ + 6e^- \rightarrow Cr_{(s)} + 3H_2O$
Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?
[Atomic mass of Cr = 52 g mol^{-1}, 1 F = 96500 C mol^{-1}] *(AI 2019)*

85. (a) The cell in which the following reaction occurs :
$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$
has E°_{cell} = 0.236 V at 298 K. Calculate the standard Gibbs energy of the cell reaction.
(Given : 1 F = 96,500 C mol^{-1}) *(NCERT Intext)*
(b) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours?
(Given : 1 F = 96,500 C mol^{-1}) *(AI 2017)*

LA (5 marks)

86. (i) State Kohlrausch's law of independent migration of ions. Write an expression for the limiting molar conductivity of acetic acid according to Kohlrausch's law.
(ii) Calculate the maximum work and log K_c for the given reaction at 298 K :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Ni^{2+}_{(aq)} + 2Ag_{(s)}$
Given : $E^\circ_{Ni^{2+}/Ni} = -0.25$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V
1 F = 96500 C mol^{-1} *(2023)*

2.6 Batteries

VSA (1 mark)

87. Define : Secondary batteries *(1/5, Delhi 2015C)* R

SA I (2 marks)

88. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. *(AI 2017)* R

89. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell. *(AI 2017)*

90. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell. *(AI 2017)*

91. What type of battery is mercury cell? Why is it more advantageous than dry cell? *(2/5, AI 2015)* U

LA (5 marks)

92. (a) The conductivity of 0·001 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate the dissociation constant if Λ°_m for acetic acid is 390.5 S cm^2 mol^{-1}.
(b) Write Nernst equation for the reaction at 25°C :
$2Al_{(s)} + 3Cu^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$
(c) What are secondary batteries? Give an example. *(2019)*

2.7 Fuel Cells

MCQ

93. Which of the following cell was used in Apollo space programme?
(a) Mercury cell (b) Daniell cell
(c) $H_2 — O_2$ Fuel cell (d) Dry cell *(2023)*

VSA (1 mark)

94. Name the cell use in hearing aids and watches. *(2020)* R

95. Name the type of cell which was used in Apollo space programme. *(2020, 1/3, AI 2014)*

96. Define : Fuel cell *(Delhi 2017, 1/5, Delhi 2015C, 2014)*

SA I (2 marks)

97. Give two advantages of fuel cells. *(2/5, 2020)*

98. Define fuel cell and write its two advantages. *(2/5, 2018)* R

99. From the given cells :
Lead storage cell, Mercury cell, Fuel cell and Dry cell
Answer the following :
(i) Which cell is used in hearing aids?
(ii) Which cell was used in Apollo space programme?
(iii) Which cell is used in automobiles and inverters?
(iv) Which cell does not have long life?
(Delhi 2016) R

100. Write two advantages of H_2—O_2 fuel cell over ordinary cell. *(2/3, Foreign 2014)*

2.8 Corrosion

VSA (1 mark)

101. Using the $E°$ values of *A* and *B* predict which is better for coating the surface of iron $\left[E°_{(Fe^{2+}/Fe)} = -0.44\ V\right]$ to prevent corrosion and why?
$E°_{(A^{2+}/A)} = -2.37\ V$; $E°_{(B^{2+}/B)} = -0.14\ V$
(AI 2016) An

CBSE Sample Questions

2.3 Nernst Equation

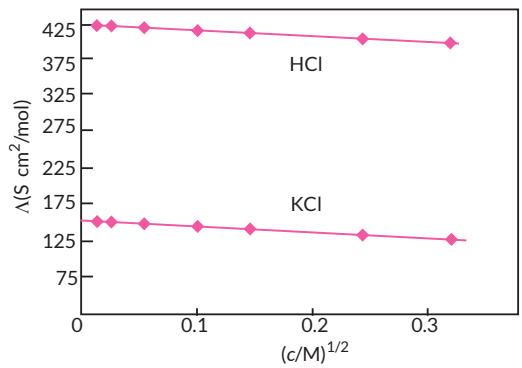
SA II (3 marks)

1. Represent the cell in which the following reaction takes place. The value of $E°$ for the cell is 1.260 V. What is the value of E_{cell}?
$2Al_{(s)} + 3Cd^{2+}\ (0.1\ M) \rightarrow 3Cd_{(s)} + 2Al^{3+}\ (0.01\ M)$
(Term II, 2021-22)

2.4 Conductance of Electrolytic Solutions

MCQ

2. The molar conductivity of CH_3COOH at infinite dilution is 390 S cm^2/mol. Using the graph and given information, the molar conductivity of CH_3COOK will be



(a) 100 S cm^2/mol (b) 115 S cm^2/mol
(c) 150 S cm^2/mol (d) 125 S cm^2/mol
(Term-II, 2021-22)

3. Which of the following option will be the limiting molar conductivity of CH_3COOH if the limiting molar conductivity of CH_3COONa is 91 S cm^2 mol^{-1}? Limiting molar conductivity for individual ions are given in the following table.

S.No.	Ions	Limiting molar conductivity / S cm^2 mol^{-1}
1.	H^+	349.6
2.	Na^+	50.1
3.	K^+	73.5
4.	OH^-	199.1

(a) 350 S cm^2 mol^{-1} (b) 375.3 S cm^2 mol^{-1}
(c) 390.5 S cm^2 mol^{-1} (d) 340.4 S cm^2 mol^{-1}
(2020-21) An

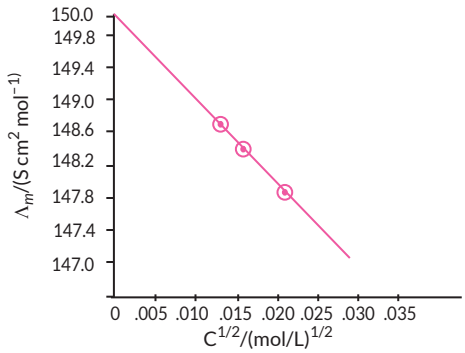
SA I (2 marks)

4. Solutions of two electrolytes '*A*' and '*B*' are diluted. The Λ_m of '*B*' increases 1.5 times while that of *A* increases 25 times. Which of the two is a strong electrolyte? Justify your answer. Graphically show the behaviour of '*A*' and '*B*'. *(Term II, 2021-22)*

LA (5 marks)

5. (i) State Kohlrausch law.
(ii) Calculate the emf of the following cell at 298 K :
$Al_{(s)}|Al^{3+}\ (0.15\ M)\ ||\ Cu^{2+}\ (0.025\ M)\ |\ Cu_{(s)}$
(Given $E°_{(Al^{3+}/Al)}$ = −1.66 V, $E°_{(Cu^{2+}/Cu)}$ = 0.34 V, log 0.15 = −0.8239, log 0.025 = −1.6020)
(2020-21)

6. (i) On the basis of $E°$ values identify which amongst the following is the strongest oxidising agent?
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-$; $E° = +1.36\ V$,
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$; $E° = +1.51\ V$
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$;
$E° = +1.33\ V$
(ii) The following figure represents variation of (Λ_m) *vs* $\sqrt{C}$ for an electrolyte. Here, Λ_m is the molar conductivity and *C* is the concentration of the electrolyte.



(a) Define molar conductivity.
(b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
(c) Determine the value of Λ_m° for the electrolyte.
(d) Show how to calculate the value of *A* for the electrolyte using the above graph. *(2020-21)*

2.5 Electrolytic Cells and Electrolysis

LA (5 marks)

7. (a) Molar conductivity of substance '*A*' is 5.9×10^3 S/m and '*B*' is 1×10^{-16} S/m. Which of the two is most likely to be copper metal and why?
(b) What is the quantity of electricity in Coulombs required to produce 4.8 g of Mg from molten $MgCl_2$? How much Ca will be produced if the same amount of electricity was passed through molten $CaCl_2$? (Atomic mass of Mg = 24 u, atomic mass of Ca = 40 u).
(c) What is the standard free energy change for the following reaction at room temperature? Is the reaction spontaneous?
$Sn_{(s)} + 2Cu^{2+}_{(aq)} \rightarrow Sn^{2+}_{(aq)} + 2Cu^{+}_{(s)}$ *(2022-23)*

2.6 Batteries

LA (5 marks)

8. (a) Why does the cell voltage of a mercury cell remain constant during its lifetime?
(b) Write the reaction occurring at anode and cathode and the products of electrolysis of aq KCl.
(c) What is the pH of HCl solution when the hydrogen gas electrode shows a potential of -0.59 V at standard temperature and pressure? *(2022-23)*

2.8 Corrosion

SA I (2 marks)

9. Corrosion is an electrochemical phenomenon. The oxygen in moist air reacts as follows:
$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$.
Write down the possible reactions for corrosion of zinc occurring at anode, cathode, and overall reaction to form a white layer of zinc hydroxide. *(2022-23)*

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. (c) : If external potential applied becomes greater than E_{cell} of electrochemical cell then the cell behaves as an electrolytic cell and the direction of flow of current is reversed.

2.

S.No.	Electrochemical cell	Electrolytic cell
1.	It is a device to convert chemical energy into electrical energy, *i.e.*, electrical energy is produced as a result of the redox reaction.	It is a device to convert electrical energy into chemical energy, *i.e.*, electrical energy is supplied to the electrolytic solution to bring about the redox reaction.
2.	It is based upon the redox reaction which is spontaneous *i.e.*, ΔG = –ve	In it redox reaction is non-spontaneous and takes place only when electrical energy is supplied *i.e.*, ΔG = +ve.

Commonly Made Mistake

- **Electrochemical cell :** Convert chemical energy into electrical energy.
- **Electrolytic cell :** Convert electrical energy into chemical energy.

3. The device which converts the chemical energy liberated during the chemical reaction to electrical energy is called electrochemical cell.
If external potential applied becomes greater than E°_{cell} of electrochemical cell then the cell behaves as an electrolytic cell and the direction of flow of current is reversed.

4. (d) : The cell can be represented as :
$Zn \mid Zn^{2+} \mid\mid Ag^+ \mid Ag$

5. (a) : If standard electrode potential of an electrode is greater than zero, then we can infer that its reduced form is more stable as compared to hydrogen gas.

6. (c) : For a spontaneous reaction, Gibb's free energy change ΔG must be negative, so E°_{cell} should be positive.
$\Delta G = -nFE^\circ_{cell}$

7. (d) : $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= +0.80 - (-0.44) = +1.24$ V

8. (b) : $Sn_{(s)} \longrightarrow Sn^{2+}_{(aq)} + 2e^-$ ...(i)

$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ ...(ii)

On multiplying equation (ii) by 2 and adding equation (i) and (ii), we get

$Sn_{(s)} + 2\,Fe^{3+}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= 0.77 - (-0.14)$
$= +0.91\ V$

$\because$ E°_{cell} is positive, so ΔG is −ve, hence spontaneous reaction.

9. $Fe \longrightarrow Fe^{2+} + 2e^-$
$2H^+ + 2e^- \longrightarrow H_2$
$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

$$= 0.44 - \frac{0\cdot0591}{2}\log\left(\frac{0.01}{1}\right)$$

$$= 0.44 + \frac{0\cdot0591}{2} \times 2$$

$E_{cell} = 0.4991\ V$

10. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= 0.40 - (-0.76)$
$= 1.16\ V$
$\Delta G^\circ = -nFE^\circ_{cell}$
$\Delta G^\circ = -2 \times 96500 \times 1.16$
$= -2,23,880\ J\ mol^{-1}$
$= -223.880\ kJ\ mol^{-1}$

11. $$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

or $$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

(i) When concentration of Cu^{2+} ions is increased, E_{cell} will increase.

(ii) When concentration of Zn^{2+} ions is increased, E_{cell} will decrease.

12. The cell can be written as

$Mg \mid Mg^{2+} \,||\, Ag^+ \mid Ag$

According to Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Mg^{2+}]}{[Ag^+]^2},\ \text{At } 25^\circ C$$

Key Points

- Metal|Metal ion (conc.) || Metal ion (conc.)|Metal
  (Salt bridge)
  By convention the electrode on which oxidation takes place is written on the L.H.S and other electrode on which reduction takes place is written on the R.H.S

13. $2Al_{(s)} + 3Ni^{2+}_{(aq.)} \longrightarrow 2Al^{3+}_{(aq.)} + 3Ni_{(s)}$

$E^\circ_{cell} = E^\circ_{Ni^{2+}/Ni} - E^\circ_{Al^{3+}/Al}$
$= -0.25 - (-1.66) = 1.41\ V$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

$$= 1.41 - \frac{0.0591}{6}\log\frac{(0.001)^2}{(0.1)^3}$$

$$= 1.41 - \frac{0.0591}{6}\log 10^{-3}$$

$$= 1.41 + \frac{0.0591}{6} \times 3 \times 1 = 1.439\ V$$

14. Given : $E^\circ_{cell} = 2.71\ V$

For the reaction, $Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

$n = 2$, $\Delta_r G^\circ = ?$

Using formula, $\Delta_r G^\circ = -nFE^\circ_{cell}$

$\Delta_r G^\circ = -2 \times 96500\ C\ mol^{-1} \times 2.71\ V$

or $\Delta_r G^\circ = -523030\ J\ mol^{-1} = -523.03\ kJ\ mol^{-1}$

15. $A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$

Here, $n = 2$

Using formula,

$$E^\circ_{cell} = \frac{0.059}{n}\log K_c$$

$$E^\circ_{cell} = \frac{0.059}{2}\log 10$$

$E^\circ_{cell} = 0.0295\ V$

16. For a general electrochemical reaction,

$aA + bB \longrightarrow cC + dD$

Nernst equation can be written as:

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Given cell :

$Zn|Zn^{2+}\ (0.001\ M)||H^+(0.01\ M)|\ H_{2(g)}\ (1\ bar)\ |\ Pt_{(s)}$

Cell reaction :

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn} = 0.00\ V - (-0.76\ V) = 0.76\ V$

$$E_{cell} = 0.76\ V - \frac{0.0591}{2}\log\frac{(0.001)}{(0.01)^2}$$

$= 0.76 - (0.0295) \times (1) = 0.76 - 0.0295 = 0.73\ V$

17. **At anode :** $Ni \rightarrow Ni^{2+} + 2e^-$

At cathode : $[Ag^+ + e^- \rightarrow Ag] \times 2$

Cell reaction : $Ni + 2Ag^+ \rightarrow Ni^{2+} + 2Ag$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= E^\circ_{Ag^+/Ag} - E^\circ_{Ni^{2+}/Ni} = 0.80\ V - (-0.25)$

$E^\circ_{cell} = 1.05\ V$

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_c$$

$$\log K_c = \frac{E^\circ_{cell} \times n}{0.0591} = \frac{1.05 \times 2}{0.0591}$$

$\log K_c = 35.53$

$K_c = \text{antilog } 35.53 = 3.38 \times 10^{35}$

$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.05 = -202650\ J\ mol^{-1}$
$= -202.65\ kJ\ mol^{-1}$

The maximum work that can be obtained = 202.65 kJ.

Answer Tips

- When a spontaneous chemical reaction occurs, the decrease in the free energy, $-\Delta G$, corresponds to the maximum possible quantity of useful work, W_{max}.

18. The cell reaction is

$Fe_{(s)} + 2H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)}$

$E^\circ_{cell} = 0.0 - (-0.44) = 0.44\ V$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

$$= 0.44 - \frac{0.0591}{2}\log\left(\frac{0.001}{(0.01)^2}\right)$$

$= 0.44 - 0.02955 = 0.41045\ V$

19. $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Here, $n = 2$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 - (-0.76) = 1.1\ V$

$1\ F = 96500\ C\ mol^{-1}$

$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 1.1 \times 96500 = -212300\ J\ mol^{-1}$

$= -212.3\ kJ\ mol^{-1}$

20. **At anode :** $Zn \rightarrow Zn^{2+} + 2e^-$

At cathode : $2Ag^+ + 2e^- \rightarrow 2Ag$

Overall reaction : $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Ag^+/Ag} - E^\circ_{Zn^{2+}/Zn}$

$= 0.80 - (-0.76) = 1.56\ V$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$= 1.56 - \frac{0.059}{2}\log\frac{0.1}{(0.01)^2} = 1.47\ V$$

21. $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} = -0.403 - (-0.763) = 0.36\ V$

$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 0.36$

$= -69480\ J\ mol^{-1} = -69.48\ kJ\ mol^{-1}$

Using formula, $\log K_c = \frac{nE^\circ_{cell}}{0.059} = \frac{2 \times 0.36}{0.059} = 12.20$

$K_c = \text{antilog } 12.20 = 1.58 \times 10^{12}$

22.

$$E = E^\circ - \frac{0.0591}{n}\log\frac{[M]}{[M^{n+}]}$$

$$= E^\circ - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

$$= -0.76 - \frac{0.0591}{2}\log\frac{1}{0.01}$$

$$= -0.76 - \frac{0.0591}{2} \times 2$$

$= -0.819\ V$

Key Points

- For pure solids or liquids or gases at one atmospheric pressure, the molar concentration (here [*M*]) is taken as unity.

23. The electrode reactions are

At anode : $Sn_{(s)} \rightarrow Sn^{2+}\ (0.004\ M) + 2e^-$

At cathode : $2H^+\ (0.02\ M) + 2e^- \rightarrow H_2\ (1\ bar)$

Net reaction :

$Sn_{(s)} + 2H^+(0.02\ M) \rightarrow Sn^{2+}(0.004\ M) + H_2\ (1\ bar)$

The Nernst equation of this cell at 25 °C

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Sn^{2+}](p_{H_2})}{[H^+]^2}$$

$E^\circ_{cell} = E^\circ_{H^+|H_2} - E^\circ_{Sn^{2+}|Sn} = 0.000\ V - (-0.14\ V) = +0.14\ V$

or, $E_{cell} = E^\circ_{cell} - 0.0296 \log \frac{0.004 \times 1}{(0.02)^2}$

$= E^\circ_{cell} - 0.0296 \log \left(\frac{0.004}{0.0004}\right)$

$= E^\circ_{cell} - 0.0296\ (\log 10)$

$= E^\circ_{cell} - 0.0296 \times 1 = E^\circ_{cell} - 0.0296$

$E_{cell} = 0.14 - 0.0296 = 0.1104\ V$

Key Points

- Remember : $E^\circ_{H^+|H_2} = 0$

24. $\Delta G^\circ = -nFE^\circ_{cell}$

$$E^\circ_{cell} = -\frac{\Delta G^\circ}{nF} = -\frac{(-43600)}{2 \times 96500} = 0.226\ V$$

$2AgCl_{(s)} + H_{2(g)}\ (1\ atm) \rightarrow 2Ag_{(s)} + 2H^+(0.1\ M) + 2Cl^-(0.1\ M)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Product]}{[Reactant]}$$

$$= 0.226 - \frac{0.0591}{2}\log\frac{(0.1)^2}{(1)}$$

$$= 0.226 - \frac{0.0591}{2}\log(10^{-2}) = 0.226 - \frac{0.0591}{2}(-2)$$

$= 0.226 + 0.0591 = 0.2851\ V$

Answer Tips

- As Cl^- is not participating in the redox reaction so Cl^- ion concentration should be ignored.

25. $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} = -0.44 - (-0.74) = 0.30\ V$

$2\ Cr + 3Fe^{2+}\ (0.1\ M) \rightarrow 2Cr^{3+}\ (0.01\ M) + 3Fe$

$$E_{cell} = 0.30 - \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.1)^3} = 0.30 + 0.01 = 0.31\ V$$

Answer Tips

- E°_{cell} = Oxidation potential at anode – oxidation potential at cathode

$= E^\circ_{ox(Anode)} - E^\circ_{ox(Cathode)}$

26. Given cell,

$2Al_{(s)} + 3Cu^{2+}\ (0.01\ M) \rightarrow 2Al^{3+}(0.01\ M) + 3Cu_{(s)}$

$E_{cell} = 1.98\ V, E^\circ_{cell} = ?$

Using Nernst equation at 298 K

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

$$1.98\ V = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{[10^{-2}]^2}{[10^{-2}]^3}$$

$1.98\ V = E°_{cell} - \frac{0.0591}{6}\log 10^2$

$1.98\ V = E°_{cell} - \frac{0.0591}{6} \times 2$

$\therefore \quad E°_{cell} = 1.98 + \frac{0.0591}{3} \simeq 2\ V$

27. $E°_{cell} = +0.80\ V - 0.77\ V = +0.03\ V$

$\Delta_r G° = -nFE°_{cell} = -1 \times 96500 \times 0.03$

$= -2895\ J\ mol^{-1} = -2.895\ kJ\ mol^{-1}$

$\Delta G° = -2.303\ RT \log K_c$

$-2895 = -2.303 \times 8.314 \times 298 \times \log K_c$

or $\log K_c = 0.5074$

$K_c = \text{Antilog}\ (0.5074) = 3.22$

28. The cell reaction can be represented as :

$Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

Given: $E^o_{cell} = +2.71\ V, T = 298\ K$

According to the Nernst equation :

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}_{(aq)}]}{[Cu^{2+}_{(aq)}]}$$

$$= 2.71 - \frac{0.0591}{2}\log\frac{0.1}{0.01} = 2.6804\ V$$

29. $Al_2O_3\ (2Al^{3+} + 3O^{2-}) \rightarrow 2Al + \frac{3}{2}O_2, n = 6e^-$

$\therefore \frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2, n = \frac{2}{3} \times 6e^- = 4e^-$

$\Delta G = 960\ kJ = 960000\ J$

Now, $\Delta G = -nFE_{cell}$

$E_{cell} = -\frac{\Delta G}{nF} = \frac{-960000}{4 \times 96500} = -2.487\ V$

Minimum potential difference needed to reduce Al_2O_3 is -2.487 V.

30. $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= 2.71 - \frac{0.0591}{2}\log\frac{0.001}{0.01} = 2.73955\ V$$

(i) If external opposing potential is less than 2.71 V then current will flow from Cu to Mg.

(ii) If external opposing potential is greater than 2.71 V then current will flow in opposite direction *i.e.* from Mg to Cu.

31. $Mg_{(s)} \mid Mg^{2+}(0.001\ M) \mid\mid Cu^{2+}(0.0001\ M) \mid Cu_{(s)}$

Reactions :

Anode : $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$

Cathode : $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Net cell reaction : $Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

$\therefore \quad n = 2$

Using Nernst equation :

$$E_{cell} = E°_{cell} - \frac{2.303RT}{nF}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

For the given cell

$E°_{cell} = E°_{cathode} - E°_{anode} = E°_{Cu^{2+}/Cu} - E°_{Mg^{2+}/Mg}$

$= 0.34\ V - (-2.37\ V) = 2.71\ V$

Given $[Mg^{2+}] = 0.001$ M, $[Cu^{2+}] = 0.0001$ M

Putting in Nernst equation at 298 K

$E_{cell} = 2.71 - \frac{0.059}{2}\log\frac{0.001}{0.0001}$

$E_{cell} = 2.71 - 0.0295 \log 10 = 2.68\ V$

$\Delta_r G = -nFE_{cell} = -2 \times 96500\ C\ mol^{-1} \times 2.68$

$= -517240\ J\ mol^{-1} = -517.24\ kJ\ mol^{-1}$

32. (b) : Unit of molar conductivity:

$$\Lambda_m = \frac{\kappa(\Omega^{-1}cm^{-1}) \times 1000(cm^3L^{-1})}{\text{Molarity}\ (molL^{-1})}$$

$= \Omega^{-1}cm^2\ mol^{-1}$ or $S\ cm^2\ mol^{-1}$.

33. (d)

Key Points

- Conductivity always decrease with decrease in concentration both for weak and strong electrolytes.

34. Conductivity of CH_3COOH (weak electrolyte) decreases with dilution because the number of current carrying particles *i.e.*, ions present per cm^3 of the solution becomes less and less on dilution.

35. The limiting molar conductivity of an electrolyte is defined as its molar conductivity when the concentration of the electrolyte in the solution approaches zero.

Conductivity of an electrolyte decreases with dilution because the number of current carrying particles *i.e.*, ions present per cm_3 of the solution becomes less and less on dilution.

36. Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

If $\lambda°_{Na^+}$ and $\lambda°_{Cl^-}$ are limiting molar conductivities of the sodium and chloride ions respectively then the limiting molar conductivity for sodium chloride is given by

$$\Lambda°_{m\ (NaCl)} = \lambda°_{Na^+} + \lambda°_{Cl^-}$$

Kohlrausch's law helps in the calculation of degree of dissociation of weak electrolyte like acetic acid.

The degree of dissociation α is given by

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$$

where, Λ_m is the molar conductivity and $\Lambda°_m$ is the limiting molar conductivity.

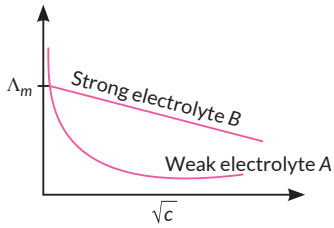
37. Molar Conductivity : Molar conductivity of a solution at a volume V is the conductance of all the ions produced from one mole of the electrolyte dissolved in $V\ cm^3$ of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them.

$\Lambda_m = \kappa V$

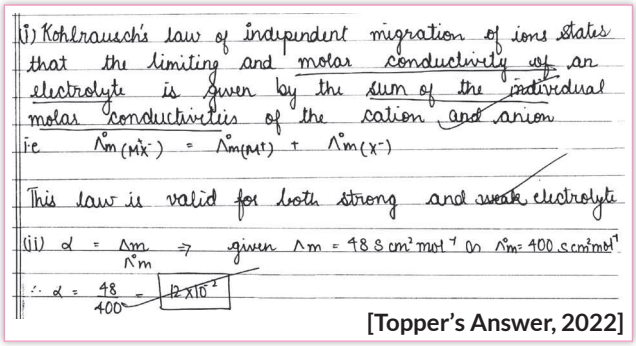
Its units are $S\ cm^2\ mol^{-1}$.

38. The molar conductivity (Λ_m) of strong electrolyte increases slowly with dilution as there is no increase in number of ions on dilution because they are already completely dissociated whereas Λ_m for weak electrolyte

increases very rapidly on dilution as the number of ions increase due to increase in dissociation. Hence, *B* is a strong electrolyte and *A* is a weak electrolyte.



39.


(i) Kohlrausch's law of independent migration of ions states that the limiting and molar conductivity of an electrolyte is given by the sum of the individual molar conductivities of the cation and anion
i.e. $\Lambda^\circ_m(MX) = \Lambda^\circ_m(M^+) + \Lambda^\circ_m(X^-)$
This law is valid for both strong and weak electrolyte
(ii) $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$ ⇒ given $\Lambda_m = 48\ S\ cm^2\ mol^{-1}$ or $\Lambda^\circ_m = 400\ S\ cm^2\ mol^{-1}$
$\therefore \alpha = \frac{48}{400} = 12 \times 10^{-2}$

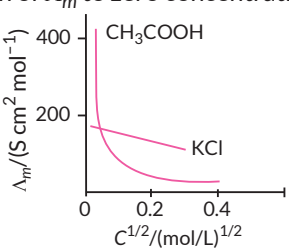
[Topper's Answer, 2022]

40. Given that, $\kappa = 7.8 \times 10^{-5}\ S\ cm^{-1}$, $M = 0.001\ M$
$\Lambda^\circ_m = 390\ S\ cm^2\ mol^{-1}$
We know that,

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{7.8 \times 10^{-5} \times 1000}{0.001} = 78\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{78}{390} = 0.2$$

41. Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation. This results in increase in the number of ions in the total volume. In case of weak electrolyte, Λ_m increases steeply on dilution at lower concentrations and does not reach a constant value even at infinite dilution. Therefore Λ°_m cannot be obtained by extrapolation of Λ_m to zero concentration.



Λ°_m for such case is obtained by using Kohlrausch law of independent migration of ions. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolytes, *i.e.*, $\Lambda^\circ_m = \upsilon_+ \lambda^\circ_+ + \upsilon_- \lambda^\circ_-$

42. (a) Molar conductivity of a solution at a volume *V* is the conductance of all the ions produced from one mole of the electrolyte dissolved in *V* cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them.

$\Lambda_m = \kappa V$

(b) Units are S $cm^2\ mol^{-1}$.

(c) Molar conductivity increases with decrease in concentration because the total volume, *V* of solution containing one mole of electrolyte also increases.

43. (a) Direct current will cause electrolysis of solution, so more ions will be produced. Hence, we use alternating current instead of direct current.

(b) Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivities of the sodium and chloride ions respectively then the limiting molar conductivity for sodium chloride is given by

$$\Lambda^\circ_{m\ (NaCl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$

(c) The cell can be represented as :
$Mg \mid Mg^{2+} \parallel Cu^{2+} \mid Cu$

44. *Y* is a weak electrolyte. As the concentration of the weak electrolyte is reduced, more of it ionises. Hence, a weak electrolyte shows a very large increase in concentration with dilution. A strong electrolyte shows only small increase in conductance with dilution, because a strong electrolyte is completely dissociated in solution so the number of ions remain constant.

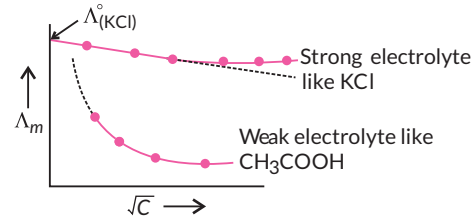
45. (i) Electrolyte *A* is a strong electrolyte while electrolyte *B* is a weak electrolyte.

(ii) For electrolyte *A*, the plot becomes linear near high dilution and thus can be extrapolated to zero concentration to get the molar conductivity at infinite dilution.

For weak electrolyte *B*, Λ_m increases steeply on dilution and extrapolation to zero concentration is not possible. Hence, molar conductivity at infinite dilution cannot be determined.

46. For a strong electrolyte it is shown by Debye-Huckel Onsager equation as follows :

$$\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$$



Here, Λ°_m = Molar conductivity at infinite dilution (Limiting molar conductivity)
Λ_m = Molar conductivity at *V*-dilution
A = Constant which depends upon nature of solvent and temperature
c = Concentration
Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ°_m and slope equal to '–*A*'.
Thus, Λ_m decreases linearly with $\sqrt{C}$, when *C* = 0,

$\Lambda_m = \Lambda^\circ_m$ and Λ°_m can be determined experimentally.

47. Degree of dissociation (α) = $\frac{\Lambda_m}{\Lambda^\circ_m}$

$$\alpha = \frac{39.05\ S\ cm^2\ mol^{-1}}{(349.68+40.9)\ S\ cm^2\ mol^{-1}} = 0.1$$

48. The fraction of the total number of molecules present in solution as ions is known as degree of dissociation.
Molar conductivity (λ_m) = $\alpha\lambda^\circ_m$
where λ°_m is the molar conductivity at infinite dilution.

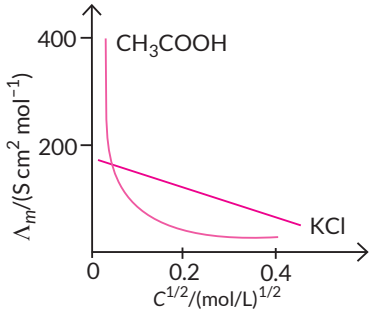
49. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa).

$$\kappa = \frac{1}{\rho} \text{ or } \kappa = G \times \frac{l}{A}$$

Hence, conductivity of a solution is defined as the conductance of a conductor of 1 cm length and having 1 cm^2 as the area of cross section. Alternatively, it may be defined as conductance of one centimetre cube of the solution of the electrolyte. Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in V cm^3 of the solution. It is represented by Λ_m.

$\Lambda_m = \kappa V$

Variation of conductivity and molar conductivity with concentration : Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. Because the number of ions per unit volume that carry the current in a solution decreases on dilution.



Molar conductivity increases with decrease in concentration because the total volume, V of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Commonly Made Mistake

- For strong electrolyte conductivity decrease with decrease in concentration while molar conductivity increase with increase in concentration.

50. Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivities of the sodium and chloride ions respectively then the limiting molar conductivity for sodium chloride is given by

$\Lambda^\circ_{m\,(NaCl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$

Conductivity of an electrolyte decreases with dilution because the number of current carrying particles *i.e.*, ions present per cm^3 of the solution becomes less and less on dilution.

51. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa).

$$\kappa = \frac{1}{\rho} \text{ or } \kappa = G \times \frac{l}{A}$$

Hence, conductivity of a solution is defined as the conductance of a conductor of 1 cm length and having 1 sq. cm as the area of cross section. Alternatively, it may be defined as conductance of one centimetre cube of the solution of the electrolyte. Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in V cm^3 of the solution. It is represented by Λ_m.

$\Lambda_m = \kappa V$

Variation of conductivity and molar conductivity with temperature : Both increase with increase in temperature as degree of ionisation increases.

52. Conductivity (κ) = $\frac{1}{R} \times G^* = \frac{1}{200} \times 1$

$= 5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$

Molar conductivity (Λ_m)

$$= \frac{\kappa \times 1000}{M} = \frac{5 \times 10^{-3} \times 1000}{0.01} = 500\ \Omega^{-1}\ cm^2\ mol^{-1}$$

53. (a) $\Delta G^\circ = nFE^\circ_{cell}$

$$E^\circ_{cell} = \frac{-\Delta G^\circ}{nF} = \frac{300 \times 1000\ J\ mol^{-1}}{2 \times 96500\ C\ mol^{-1}} = 1.55\ V$$

(b) $\Lambda^\circ_m (MgCl_2) = \lambda^\circ_m (Mg^{2+}) + 2\lambda^\circ_m (Cl^-)$

$= 106\ S\ cm^2\ mol^{-1} + 2 \times 76.3\ S\ cm^2\ mol^{-1}$

$= 258.6\ S\ cm^2\ mol^{-1}$

54. Using formula, $\Lambda_m = \frac{\kappa \times 1000}{C}$

Given, $\kappa = 3.905 \times 10^{-5}\ S\ cm^{-1}$
$C = 0.001\ mol\ L^{-1}$

$$\therefore \Lambda_m = \frac{3.905 \times 10^{-5} \times 1000}{0.001} = 39.05\ S\ cm^2\ mol^{-1}$$

The degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{39.05}{390.5} = 0.1$

$[\because \Lambda^\circ_m = 349.6 + 40.9 = 390.5\ S\ cm^2\ mol^{-1}]$

55. Given : Conductivity, $\kappa = 8 \times 10^{-5}\ S\ cm^{-1}$
Molarity, $C = 0.002\ M = 0.002\ mol\ L^{-1}$
Using formula, $\Lambda^c_m = \frac{1000 \times \kappa}{C}$

$$\Lambda^c_m = \frac{1000 \times 8 \times 10^{-5}}{0.002} = 40\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{40}{404} = 0.099$$

56. (i) Silver wire at 30 °C allows greater conduction of electricity than 60 °C because with increase in temperature metallic conduction decreases due to vibration of kernels.
(ii) 0.1 M acetic acid solution allows greater conduction of electricity because with dilution degree of dissociation increases and hence, number of ions increases.
(iii) KCl solution at 50° C will have greater conductance. This is because ionic mobilities increases with increase in temperature.

Commonly Made Mistake

➲ In solid metals, conduction decreases with increase in temperature while in solution conductivity increases with increase in temperature.

57. Given : $a = 0.625\ cm^2$, $l = 50\ cm$
$R = 5 \times 10^3$ ohm, $M = 0.05$ M

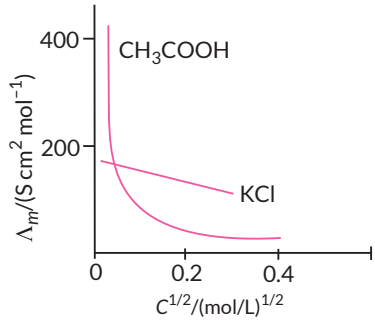
$$\text{Resistivity, } \rho = R \times \frac{A}{l} = 5 \times 10^3 \times \frac{0.625}{50} \text{ ohm cm}$$
$$= 62.5 \text{ ohm cm}$$

$$\text{Conductivity, } \kappa = \frac{1}{\rho} = \frac{1}{62.5} = 0.016 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{M}$$
$$= \frac{0.016 \times 1000}{0.05} = 320 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

58. (a) $E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Zn^{2+}/Zn}$
$= 0.80 + 0.76 = 1.56$ V
$\Delta_r G^\circ = -nFE^\circ$
$\Delta_r G^\circ = -2 \times 96500 \times 1.56$
$= 301080 \text{ J mol}^{-1} = 301.080 \text{ kJ mol}^{-1}$

(b) For strong electrolytes the plot between Λ_m and $\sqrt{C}$ is a straight line with intercept equal to Λ°_m and slope equal to $-A$. Λ°_m for these can be obtained by extrapolation of Λ_m to zero concentration.



Λ°_m for weak electrolyte cannot be obtained by entrapolaration of graph at zero concentration. Λ°_m for such case is obtained by using Kohlrausch law of independent migration of ions. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolytes, *i.e.*, $\Lambda^\circ_m = \upsilon_+ \lambda^\circ_+ + \upsilon_- \lambda^\circ_-$

59. Given : Conductivity, $\kappa = 0.0248\ S\ cm^{-1}$
Molarity, $C = 0.20$ M $= 0.20\ mol\ L^{-1}$

$$\text{Using formula, } \Lambda^c_m = \frac{1000 \times \kappa}{C}$$

$$\Lambda^c_m = \frac{1000 \times 0.0248}{0.20} = 124\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{124}{73.5 + 76.5} = 0.82$$

60. Resistance of 0.1 M KCl solution $R = 100\ \Omega$
Conductivity $\kappa = 1.29\ S\ m^{-1}$
Cell constant $G^* = \kappa \times R = 1.29 \times 100 = 129\ m^{-1}$
Resistance of 0.02 M KCl solution, $R = 520\ \Omega$

$$\text{Conductivity, } \kappa = \frac{\text{cell constant}}{R} = \frac{129\ m^{-1}}{520\ \Omega} = 0.248\ S\ m^{-1}$$

Concentration, $C = 0.02\ mol\ L^{-1}$
$= 1000 \times 0.02\ mol\ m^{-3} = 20\ mol\ m^{-3}$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa}{C} = \frac{0.248\ S\ m^{-1}}{20\ mol\ m^{-3}}$$
$$= 0.0124\ S\ m^2\ mol^{-1}$$

61. (a) Conductivity of an electrolyte decreases with dilution because the number of current carrying particles *i.e.*, ions present per cm^3 of the solution becomes less and less on dilution.
Molar conductivity increases with decrease in concentration because the total volume, V of solution containing one mole of electrolyte also increases.

(b) Degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$

Given, $\Lambda^\circ_m = 150.0\ S\ cm^2\ mol^{-1}$
$\Lambda_m = 141.0\ S\ cm^2\ mol^{-1}$

$$\therefore \quad \alpha = \frac{141}{150} = 0.94 \text{ or } 94\%$$

(c) H^+ ion is smaller than K^+ ion. Since, smaller the cation, higher the molar conductivity, hence for the same concentration of HCl and KCl, molar conductivity of HCl is higher than that of KCl.

62. (a) The half cell reactions are :
At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$
At cathode : $2Ag^+ + 2e^- \longrightarrow 2Ag$
So, silver plate is acting as cathode where reduction is taking place.
(b) The function of salt bridge in an electrochemical cell is to maintain electrical neutrality in solutions and prevent voltage drop. If the salt bridge is removed voltage will drop to zero and no current will flow.
(c) If external potential applied becomes greater than E°_{cell} of electrochemical cell then it behaves as an electrolytic cell and the direction of flow of current is reversed.
(d) (i) When E_{cell} is equal to zero, there will be a condition of equilibrium in the cell. So, the concentrations of Zn^{2+} and Ag^+ will become constant.
(ii) Conductivity of the solution decreases with dilution because the number of ions per unit volume that carry the current in solution decreases with dilution.

OR

(d) Given that, $\lambda_m = 138.9\ S\ cm^2\ mol^{-1}$,
Concentration = 1.5 M, $\kappa = ?$

$$\lambda_m = \frac{\kappa \times 1000}{M} \quad \Rightarrow \quad \kappa = \frac{\lambda_m \times M}{1000}$$

$k = \frac{138.9\ S\,cm^2\,mol^{-1} \times 1.5M}{1000} = 0.208\ S\,cm^{-1}$

63. (i) $C = 0.02$ M

$r = \frac{d}{2} = \frac{1.40}{2}\ cm = 0.70\ cm$

$l = 44$ cm, $R = 5.00 \times 10^3\ \Omega$

As we know that,

$R = \rho\frac{l}{A} \Rightarrow 5.00\times10^3 = \rho \times \frac{44}{\pi(0.70)^2}$

$\rho = \frac{5.00\times10^3\times3.14\times(0.70)^2\times10^{-2}}{44}$

$= 174.8\ \Omega\,cm$

Conductivity, $\kappa = \frac{1}{\rho} = \frac{1}{174.8} = 5.72\times10^{-3}\Omega^{-1}cm^{-1}$

Molar conductivity,

$\Lambda_m = \kappa \times \frac{1000}{\text{Molarity}} = \frac{5.72\times1000\times10^{-3}}{0.02} = 2,86\,Scm^2\,mol^{-1}$

(ii) $Ni|Ni^{2+}||Ag^+|Ag$

(i) Silver electrode is positively charged.

(ii) Electrons are the carriers of the current in the outer circuit.

64. (a) $2Al + 3Ni^{2+}(0.1\ M) \rightarrow 2Al^{3+}(0.01\ M) + 3Ni$

$E^\circ_{cell} = 1.41$ V

The cell can be represent as :

$Al\ |\ Al^{3+}(0.01\ M)\ ||\ Ni^{2+}(0.1\ M)\ |\ Ni$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$

$= 1.41 - \frac{0.0591}{n}\log\frac{(0.01)^2}{(0.1)^3}$

$= 1.41 - \frac{0.0591}{6}\log10^{-1}$

$= 1.41 + \frac{0.0591}{6} = 1.419$ V

(b) For weak electrolytes molar conductivity decrease with increase in concentration. As on low concentration (or on dilution) ionisation increases for weak electrolytes hence molar conductivity increases on dilution.

While the molar conductivity of strong electrolytes increases with increase in concentration as number of ions increases on increasing concentration.

For strong electrolyte, $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$

Thus Λ_m increase with increase in concentration.

Limiting molar conductivity for weak electrolytes is obtained by using kohlrauhch law of independent migration of ions. The law states that limiting molar conductivity of on electrolyte can be represent as the sum of the individual contributions of an anion and cation of the electrolyte i.e.,

$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$

65. (b): When concentrated brine *i.e.* aqueous solution of NaCl is electrolysed, products are chlorine at anode and hydrogen at cathode.

At cathode:

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

At anode :

$2Cl^-_{(aq.)} \rightarrow Cl_{2(g)} + 2e^-$

66. $\overset{+7}{MnO_4^-} + 5e^- \longrightarrow Mn^{2+}$

As $5e^-$ are needed to reduce 1 mol of MnO_4^- to Mn^{2+} thus chnage required is 5 Faraday.

Answer Tips

➲ For calculating charge required calculate number of electrons need for the change.

67. $\overset{-2}{H_2O} \longrightarrow H_2 + \frac{1}{2}\overset{0}{O_2}$,

charge required to oxidised 1 mol of H_2O is 2F

$= 2 \times 96500 = 193000$ C

68. The reaction at anode with lower value of E° is preferred *i.e.*, O_2 gas should be liberated but on account of overpotential of oxygen, reaction preferred at anode is

$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$

i.e., Cl_2 gas is liberated at anode in the electrolysis of aq. NaCl.

69. The species that get reduced at cathode is the one having higher value of standard reduction potential. Hence, the reaction that will occur at cathode is $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$.

70. $\underset{1\,mol}{Zn^{2+}_{(aq)}} + \underset{2\,mol}{2e^-} \longrightarrow Zn_{(s)}$

One mole of Zn^{2+} requires 2 moles of electrons for reduction *i.e.*

$Q = 2 \times F = 2 \times 96500 = 193000$ C

71. The species that get reduced at cathode is the one which have higher value of standard reduction potential. Hence, the reaction that will occur at cathode is

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

72. Faraday's first law of electrolysis : During electrolysis the amount of any substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte *i.e.*,

$w \propto Q$ or $w \propto I \times t$ $[\because\ Q = I \times t]$

$w = Z \times I \times t$

where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.

73. (i) $\Delta G^\circ = -nFE^\circ_{cell}$ (nF = amount of charge passed)

If ΔG is negative, *i.e.* E° is positive then the reaction will be spontaneous.

(ii) According to Faraday's first law of electrolysis, "weight of ions deposited on an electrode of an electrolytic cell is directly proportional to the quantity of electricity passed" *i.e.*,

$w \propto Q$ or $w = ZQ = ZIt$

where, Q = quantity of electricity (in coulombs)

I = current (in amperes), t = time (in second)

Z = electrochemical equivalent of material deposited on the electrode.

74. In aqueous solution, $CuCl_2$ ionises into

$CuCl_2 \rightarrow Cu^{2+} + 2Cl^-$

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

At anode : $2Cl^- \rightarrow Cl_2 + 2e^-$

At the cathode, the copper ion will be deposited because it has a higher reduction potential than the water molecule. At the anode, the lower electrode potential value will be preferred but due to over potential of oxygen, chloride ion gets oxidized at the anode.

75. (a) $CuSO_{4(aq)} \rightarrow Cu^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

At cathode: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

At anode : $H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^-$

(b) At the cathode the following reduction reactions compete to take place :

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$; $E° = 0.80$ V

$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$; $E° = 0.00$ V

The reaction with a higher value of $E°$ takes place at the cathode. Therefore, the deposition of silver will take place. Since, Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH_- ions having a lower discharge potential get preference and decompose to liberate O_2.

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

76. $\underset{1\text{ mole}}{Fe^{3+}} + \underset{1e^-}{1e^-} \rightarrow Fe^{2+}$

1 mole of Fe^{3+} requires 1 mole of electrons for reduction.

3 moles of Fe^{3+} requires 3 moles of electrons for reduction.

i.e., $Q = 3 \times F$

$Q = 3 \times 96500$

$I = 2A$

$I = \frac{Q}{t}$

$t = \frac{Q}{I} = \frac{289500}{2} = 144750$ s

77. The species that get reduced at cathode is the one having higher value of standard reduction potential.

Hence, the reaction that will occur at cathode is

$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$; $E° = 0{\cdot}00$ V

The species that get oxidised at anode is the one having lower value of $E°$. Thus

$2H_2O \longrightarrow O_{2(g)} + 4H^+ + 4e^-$

should take place but on account of overpotential of oxygen reaction preferred at anode is

$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$; $E° = +1{\cdot}36$ V

78. Given : $I = 2$ A, $t = 15$ min $= 15 \times 60$ s $= 900$ s, $w = ?$

$Q = I \times t = 2 \times 900 = 1800$ C

Reaction for deposition of Ag is as follows :

$\underset{\underset{1 \times 96500\text{ C}}{1\text{ F}}}{Ag^+ + 1e^-} \rightarrow \underset{108\text{ g}}{\underset{1\text{ mol}}{Ag}}$

Thus, 1 × 96500 C of electricity is required to deposit 108 g of Ag.

$\therefore$ 1800 C of electricity would deposit

$= \frac{108 \times 1800}{1 \times 96500} = 2.014$ g of Ag

79. Faraday's first law of electrolysis : During electrolysis the amount of any substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte *i.e.*,

$w \propto Q$ or $w \propto I \times t$ [$\because Q = I \times t$]

$w = Z \times I \times t$

where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.

The electrode reaction is $Cu^{2+} + 2e^- \rightarrow Cu$

$\therefore$ Quantity of charge required for reduction of 1 mol of $Cu^{2+} = 2F = 2 \times 96500 = 193000$ C

80. Given : Current $I = 5$ A; $t = 20 \times 60$ s, $w = ?$

$Q = I \times t = 5 \times 20 \times 60 = 6000$ C

Reaction for deposition of Ni,

$\underset{\underset{2 \times 96500\text{ C}}{2\text{ mol}}}{Ni^{2+} + 2e^-} \longrightarrow \underset{58.7\text{ g}}{\underset{1\text{ mol}}{Ni}}$

Thus, 2 × 96500 C of electricity produces 58.7 g Ni.

$\therefore$ 6000 C of electricity would produce

$= \frac{58.7 \times 6000}{2 \times 96500} = 1.825$ g

81. (i) At the cathode the following reduction reactions compete to take place :

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$; $E° = 0.80$ V

$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$; $E° = 0.00$ V

The reaction with a higher value of $E°$ takes place at the cathode. Therefore, the deposition of silver will take place. Since, Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH_- ions having a lower discharge potential get preference and decompose to liberate O_2.

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

(ii) At the cathode, the following reduction reaction occurs to produce H_2 gas.

$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$

At the anode, the following processes are possible :

$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$; $E° = +1.23$ V ...(i)

$2SO^{2-}_{4(aq)} \rightarrow S_2O^{2-}_{8(aq)} + 2e^-$; $E° = +1.96$ V ...(ii)

For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas but for concentrated sulphuric acid, (ii) occurs.

82. According to first law of electrolysis,

$w = ZIt$

$w = \frac{\text{Eq. wt.}}{F} \times It$

$w_{Cu} = 2$ g

$I = 2$ A

$2 = \frac{31.75}{96500} \times 2 \times t \Rightarrow t = \frac{96500 \times 2}{2 \times 31.75} = 3040$ sec

Eq. w.t of $Cu^{2+} = 31.75$

According to second law of electrolysis,

$$\frac{\text{Mass of Zn deposited}}{\text{Mass of Cu deposited}} = \frac{\text{Eq. wt. of Zn}}{\text{Eq. wt. of Cu}}$$

$$\frac{w_{Zn}}{2} = \frac{32.5}{31.75}$$

$$w_{Zn} = \frac{32.5 \times 2}{31.75} = 2.047 \text{ g}$$

83. According to Faraday's first law of electrolysis,
mass of substance deposited ∝ quantity of electricity passed

$$\Rightarrow \quad W = ZQ = \frac{\text{Eq. wt.}}{F} \times Q$$

$$\Rightarrow \quad 2.8 = \frac{28}{96500} \times Q$$

$$\Rightarrow \quad Q = \frac{2.8 \times 96500}{28} = 9650 \text{ C}$$

$$\text{Now } Q = It \quad \Rightarrow \quad t = \frac{Q}{I} = \frac{9650}{2} = 4825 \text{ s}$$

According to Faraday's second law of electrolysis,

$$\frac{\text{Mass of Fe deposited}}{\text{Mass of Zn deposited}} = \frac{\text{Eq.wt.of Fe}}{\text{Eq.wt.of Zn}}$$

$$\Rightarrow \quad \frac{2.8}{\text{Mass of Zn deposited}} = \frac{28}{32.65}$$

$$\Rightarrow \quad \text{Mass of Zn deposited} = \frac{2.8}{28} \times 32.65 = 3.265 \text{ g}$$

84. Charge = 24,000 coulombs
According to reaction, $Cr^{6+} + 6e^- \rightarrow Cr_{(s)}$
We require 6F or 6 × 96500 C to deposit 1 mole or 52 g of Cr.
For 24,000 C, the mass of Cr deposited

$$= \frac{52 \times 24{,}000}{6 \times 96500} = 2.15 \text{ g}$$

According to Faraday's first law of electrolysis,

$$\frac{w_1}{w_2} = \frac{Q_1}{Q_2} \quad \text{or} \quad \frac{2.15}{1.5} = \frac{24{,}000}{12.5 \times t}$$

$w = ZIt$

$$1.5 = \frac{52}{6 \times 96500} \times 12.5 \times t \Rightarrow t = \frac{6 \times 1.5 \times 96500}{52 \times 12.5} = 1336.15 \text{ s}$$

85. (a) $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ and $2I^- \longrightarrow I_2 + 2e^-$
Hence, for the given cell reaction, $n = 2$
$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 0.236 = -45.55 \text{ kJ mol}^{-1}$
(b) Given, $I = 0.5$ A, $t = 2$ hrs.
Number of electrons = ?
Total charge (Q) = $I \times t = 0.5 \times 2 \times 60 \times 60 = 3600$ C

$$\therefore \quad \text{Number of electrons} = \frac{\text{Total charge}}{\text{Charge of one electron}} = \frac{3600}{1.6 \times 10^{-19}} = 2.25 \times 10^{22} \text{ electrons}$$

86. (i) It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
Expression for the limiting molar conductivity of acetic acid is

$$\Lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

(ii) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Ag^+/Ag} - E^\circ_{Ni^{2+}/Ni}$
$= +0.80 \text{ V} - (-0.25 \text{ V})$
$= 1.05 \text{ V}$
Maximum work = $\Delta G^\circ = -nFE^\circ_{cell}$
$= -2 \times 96500 \times 1.05$
$= -202650 \text{ J mol}^{-1}$
$= -202.65 \text{ kJ mol}^{-1}$
$\Delta G^\circ = -RT \ln K_c = -202650 \text{ J mol}^{-1}$
$8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K} \ln K_c = 202650 \text{ J mol}^{-1}$
$\ln K_c = 81.79$
$2.303 \log K_c = 81.79$
$\log K_c = 35.5145$

87. The batteries which can be recharged again and again are called as secondary batteries. *e.g.*, lead storage battery.

88. The mercury cell is generally used in hearing aids.
Reaction at cathode :

$$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$$

Reaction at anode :

$$Zn(Hg) + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$$

89. The cell which is generally used in inverters is secondary cell *i.e.*, lead storage battery.
At cathode : $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$
At anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$

90. Mercury cell is generally used in transistors.
At cathode : $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$
At anode : $Zn(Hg) + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

91. Mercury cell is a primary battery. Hence, it can be used only once and cannot be recharged.
Advantage : The cell potential remains constant during its life time. Hence, it is useful for devices requiring constant current *e.g.*, hearing aids and watches.

92. (a) $\kappa = 4.95 \times 10^{-5} \text{ S cm}^{-1}$, $M = 0.001$ M
$\Lambda^\circ_m = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$
We know that

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{4.95 \times 10^{-5} \times 1000}{0.001} = 49.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{49.5}{390.5} = 0.1267$$

$$K_c = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times 0.1267 \times 0.1267}{(1 - 0.1267)} = 1.82 \times 10^{-5}$$

(b) $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{6} \log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

(c) The batteries which can be recharged again and again are called as secondary batteries. *e.g.*, lead storage battery.

93. (c) : The H_2-O_2 fuel cell was used for producing electricity in Apollo space programme. The water vapours produced were condensed and added to drinking water supply for astronauts.

94. Mercury cell is used for low current devices like hearing aids and watches.

Key Points

- Mercury cell is used in waters and hearing aids because their potential remains constant throughout their life.

95. The hydrogen oxygen fuel cell was used in Apollo space programme.

96. Those galvanic cells which give us direct electrical energy by the combustion of fuels like hydrogen, methane, methanol, etc. are called fuel cells.

97. The two advantages of fuel cells are :
(i) They produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%.
(ii) They are pollution free.

98. Those galvanic cells which give us direct electrical energy by the combustion of fuels like hydrogen, methane, methanol, etc. are called fuel cells.
The two advantages of fuel cells are :
(i) They produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%.
(ii) They are pollution free.

99. (i) Mercury cell is used for low current devices like watches and hearing aids.
(ii) The hydrogen oxygen fuel cell was used in Apollo space programme.
(iii) Lead storage battery is used in automobiles and inverters.
(iv) Dry cell.

100. (i) It is pollution free.
(ii) It has high efficiency of 70 - 75% and its rate can be controlled.

101. Metals of lower electrode potential value when connected with iron protect it from oxidation and prevent corrosion. Hence, coating of metal *A* having lower electrode potential will be better than *B* which has higher $E°_{(B^{2+}/B)}$ = (– 0.14 V).

CBSE Sample Questions

1. $Al\,|\,Al^{3+}(0.01\ M)\,||\,Cd^{2+}(0.1\ M)\,|\,Cd$ **(1/2)**

$2Al_{(s)} + 3Cd^{2+}\,(0.1\ M) \rightarrow 3Cd_{(s)} + 2Al^{3+}\,(0.01\ M)$

$E_{cell} = E°_{cell} - \dfrac{0.059}{n}\log\dfrac{[Al^{3+}]^2}{[Cd^{2+}]^3}$ **(1/2)**

$E_{cell} = 1.26 - \dfrac{0.059}{6}\log\dfrac{(0.01)^2}{(0.1)^3}$ **(1/2)**

$= 1.26 - \dfrac{0.059}{6}(-1)$ **(1)**

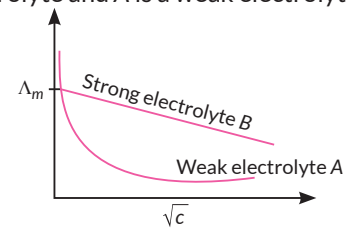
$= 1.26 + 0.0098 = 1.269\ V \approx 1.27\ V$ **(1/2)**

2. **(b) :** $\Lambda°_{CH_3COOK} = \Lambda°_{CH_3COOH} + \Lambda°_{KCl} - \Lambda°_{HCl}$
$= 390 + 150 - 425 = 115\ S\ cm^2/mol$ **(1)**

3. **(c) :** Limiting molar conductivity of CH_3COOH can be calculated as

$\Lambda°_{CH_3COOH} = \lambda°_{CH_3COONa} + \lambda°_{H^+} - \lambda°_{Na^+}$
$= 91 + 349.6 - 50.1$
$= 440.6 - 50.1 = 390.5\ S\ cm^2\ mol^{-1}$ **(1)**

4. The molar conductivity(Λ_m) of strong electrolyte increases slowly with dilution as there is no increase in number of ions on dilution because they are already completely dissociated whereas Λ_m for weak electrolyte increases very rapidly on dilution as the number of ions increase due to increase in dissociation. Hence, *B* is a strong electrolyte and *A* is a weak electrolyte. **(1)**



(1)

5. (i) **Kohlrausch's law :** It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. **(1)**

If $\lambda°_{Na^+}$ and $\lambda°_{Cl^-}$ are limiting molar conductivities of the sodium and chloride ions respectively then the limiting molar conductivity for sodium chloride is given by

$\Lambda°_{m(NaCl)} = \lambda°_{Na^+} + \lambda°_{Cl^-}$

(ii) $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}\ ;\ E°_{Cu^{2+}/Cu} = 0.34\ V$ (At cathode)
$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-;\ E°_{Al^{3+}/Al} = -1.66\ V$ (At anode)
$2Al_{(s)} + 3Cu^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$ (Overall reaction)
(1/2)

$E°_{cell} = E°_{cathode} - E°_{anode} = 0.34 - (-1.66) = 2.00\ V$ **(1/2)**

$E_{cell} = E°_{cell} - \dfrac{0.059}{n}\log\dfrac{[Al^{3+}]^2}{[Cu^{2+}]^3}$ **(1)**

$= 2.00 - \dfrac{0.059}{6}\log\dfrac{(0.15)^2}{(0.025)^3}$ $(\because\ n = 6)$ **(1)**

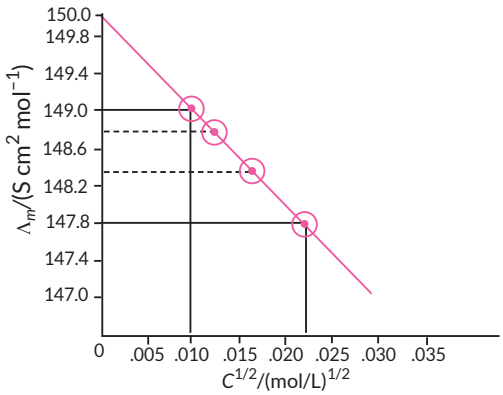
$= 2.00 - \dfrac{0.059}{6}(2\log 0.15 - 3\log 0.025)$

$= 2.00 - \dfrac{0.059}{6}(-1.6478 - (-4.806))\ = 1.9689\ V$ **(1)**

6. (i) MnO_4^- is the strongest oxidising agent because it has maximum positive $E°$ value. **(1)**
(ii) (a) Molar conductivity of a solution at a dilution *V* is the conductance of all the ions produced from one mole of the electrolyte dissolved in *V* cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them, *i.e.*, $\Lambda_m = \kappa V_m$ **(1)**
(b) Electrolyte is a strong electrolyte. Molar conductivity (Λ_m) increases slowly with dilution. **(1)**
(c) $\Lambda_m = \Lambda°_m - AC^{1/2}$ **(1)**

$\Lambda°_m$ is equal to intercept on y-axis of the graph.
Therefore $\Lambda°_m = 150\ S\ cm^2\ mol^{-1}$

(d)



A = – slope = – (149 – 147.8/0.010 – 0.022)
= 100 S cm^2 mol^{-1}/(mol/L^{-1})$^{1/2}$ **(1)**

7. (a) "A" is copper metal as metals have high value of conductivity. **(1)**

(b) $Mg^{2+} + 2e^- \longrightarrow Mg$

1 mole of magnesium ions gain 2 moles of electrons or 2F to form 1 mole of Mg. 24 g Mg requires 2F electricity.

4.8 g Mg requires $2 \times \frac{4.8}{24} = 0.4F = 0.4 \times 96500 = 38600C$ **(1)**

$Ca^{2+} + 2e^- \rightarrow Ca$

2 F electricity is required to produce 1 mole or 40 g Ca.

0.4 F electricity will produce 8 g Ca. **(1)**

(c) F = 96500C, n = 2,

$Sn^{2+}_{(aq)} + 2e^- \longrightarrow Sn_{(s)}$; $E°$ – 0.14 V

$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^{+}_{(aq)}$; $E°$ = 0.15 V

$E°_{cell} = E°_{Cathode} - E°_{Anode}$
= 0.15 – (–0.14) = 0.29 V

$\Delta G° = -nFE°_{cell} = 2 \times 96500 \times 0.29 = 55970$ J/mol **(1)**

8. (a) The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its lifetime. **(1)**

(b) $KCl_{(aq)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$

Cathode: $H_2O_{(l)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$ **(1/2)**

Anode: $Cl^-_{(aq)} \longrightarrow \frac{1}{2}Cl_{2(aq)} + e^-$ **(1/2)**

Net reaction: $KCl_{(aq)} + H_2O_{(l)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)} + \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)}$ **(1)**

(c) Given, potential of hydrogen gas electrode = –0.59 V

Electrode reaction: $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

Applying Nernst equation,

$E_{(H^+/H_2)} = E°_{(H^+/H_2)} - \frac{0.059}{n}\log\frac{[H_2]^{1/2}}{[H^+]}$ **(1)**

$E°_{(H^+/H_2)}$ = 0 V

$E_{(H^+/H_2)}$ = –0.59 V

n = 1

$[H_2]$ = 1 bar

–0.59 = 0 – 0.059 (– log $[H^+]$) **(1/2)**

–0.59 = – 0.059pH **(1/2)**

∴ pH = 10

9. Anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ **(1/2)**

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$ **(1/2)**

Overall: $2Zn_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Zn^{2+}_{(aq)} + 4OH^-_{(aq)}$

$2Zn_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2[Zn(OH)_2]_{(ppt.)}$ **(1)**

Self Assessment

Case Based Questions (5 marks)

1. **Read the passage given below and answer the following questions :**
All chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules are present in a few gram of any chemical compound varying with their atomic/molecular masses. To handle such large number conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrode. The amount of products formed can be calculated by using mole concept.
(i) The total number of moles of chlorine gas evolved is
(a) 0.5 (b) 1.0 (c) 1.5 (d) 1.9
(ii) If cathode is a Hg (Atomic mass = 200.59 g/mol) electrode, then the maximum weight of amalgam formed from this solution is
(a) 300 g (b) 446 g (c) 396 g (d) 296 g
(iii) The total charge (coulomb) required for complete electrolysis is
(a) 186000 (b) 24125 (c) 48296 (d) 193000
(iv) In the electrolysis of aqueous NaCl, the number of moles of electrons involved are
(a) 2 (b) 1 (c) 3 (d) 4
(v) In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?
(a) H_2 gas (b) Cl_2 gas
(c) O_2 gas (d) None of these

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

2. **Assertion :** Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
Reason : For weak electrolytes degree of dissociation increases with dilution of solution.

3. **Assertion :** Electrolysis of NaCl solution gives chlorine at anode instead of O_2.
Reason : Formation of oxygen at anode requires overvoltage.

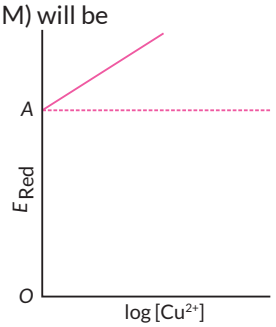
Multiple Choice Questions (1 mark)

4. Among the following, which will be the best conductor of electricity?
(a) 1 M Acetic acid (b) 1 M Sulphuric acid
(c) 1 M Boric acid (d) 1 M Formic acid

5. The molar conductance of 0.001 M acetic acid is 50 $ohm^{-1}\ cm^2\ mol^{-1}$. The maximum value of molar conductance is 250 $ohm^{-1}\ cm^2\ mol^{-1}$. What is its degree of ionization?
(a) 0.5% (b) 2% (c) 20% (d) 22%

6. The electrode reactions for charging of a lead battery are
$PbSO_4 + 2e^- \longrightarrow SO_4^{2-} + Pb$
$PbSO_4 + 2H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$
The electrolyte in the battery is an aqueous solution of sulphuric acid after the battery has been charged
(a) the sulphuric acid will be more concentrated
(b) the sulphuric acid will be less concentrated
(c) the concentration of sulphuric acid will be unchanged
(d) sulphuric acid will have been completely decomposed.

7. $Cu^{2+} + 2e^- \longrightarrow Cu$; log $[Cu^{2+}]$ *vs* E_{Red} graph is of the type as shown in figure where OA = 0.34 V. Then electrode potential of the half cell of $Cu \mid Cu^{2+}(0.1\ M)$ will be



(a) $-0.34 + \frac{0.0591}{2}$ (b) $0.34 + \frac{0.0531}{2}$ V
(c) 0.34 V (d) none of these.

8. Standard reduction potentials of the half reactions are given below :
$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$; $E° = +2.85$ V
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$; $E° = +1.36$ V
$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$; $E° = +1.06$ V
$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$; $E° = +0.53$ V
The strongest oxidising and reducing agents respectively are
(a) F_2 and I^- (b) Br_2 and Cl^-
(c) Cl_2 and Br^- (d) Cl_2 and I_2

VSA Type Questions (1 mark)

9. Arrange the following metals in the order in which they displace each other from the solution of their salts.
Al, Cu, Fe, Mg and Zn.

10. What is the necessity to use a salt bridge in a Galvanic cell?

11. Under what condition $E_{cell} = 0$ or $\Delta_r G = 0$?

OR

Express the relation among the conductivity of solution in the cell, the cell constant and the resistance of solution in the cell.

SA I Type Questions (2 marks)

12. Value of standard electrode potential for the oxidation of Cl^- ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water?

13. How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours?

14. Mention the reactions occurring at (i) anode, (ii) cathode, during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation?

OR

Give reasons for the following :
(i) Rusting of iron is quicker in saline water than in ordinary water.
(ii) Aluminium metal cannot be produced by the electrolysis of aqueous solution of aluminium salt.

15. Zinc can reduce hydrogen ion but copper cannot. Why?

16. Mention few applications of electrochemical series.

SA II Type Questions (3 marks)

17. Depict the galvanic cell in which the reaction $Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ takes place.
Further show:
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.

18. (a) What is corrosion? Explain the electrochemical theory of rusting of iron and write the reactions involved in the rusting of iron.
(b) Which reference electrode is used to measure the electrode potential of other electrodes?

19. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol.

20. How does the molar conductance increase on diluting the solution of a weak electrolyte? Electrolytic conductivity of 0.30 M solution of KCl at 295 K is 3.72×10^{-2} S cm^{-1}. Calculate the molar conductivity.

OR

Account for the following :
(i) Alkaline medium inhibits the rusting of iron.
(ii) Iron does not rust even if the zinc coating is broken in a galvanized iron pipe.

Cased Based Question (5 marks)

21. **Read the passage given below and answer the following questions :**
The electrochemical cell shown below is concentration cell.
$M|M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) $||M^{2+}$ (0.001 mol dm^{-3}) $|M$
The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.
(i) Calculate the solubility product (K_{sp} in mol^3 dm^{-9}) of MX_2 at 298 K based on the information available for the given concentration cell.
(Take $2.303 \times R \times 298/F = 0.059$) (1 Mark)
(ii) Calculate the value of ΔG (in kJ mol^{-1}) for the given cell. (Take 1 F = 96500 C mol^{-1}) (1 Mark)
(iii) The standard electrode potential ($E°$) for OCl^-/Cl^- and $Cl^-/\frac{1}{2}Cl_2$ respectively are 0.94 V and – 1.36 V. What will be the $E°$ value for $OCl^-/\frac{1}{2}Cl_2$? (2 Marks)

OR

Calculate the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag|Ag^+$ (satd. Ag_2CrO_4 soln) $||Ag^+$ (0.1 M) $|Ag$ is 0.164 V at 298 K. (2 Marks)

LA Type Questions (5 marks)

22. Answer the following :
(a) Suggest a way to determine Λ°_m value of water.
(b) The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant.
Given
$\lambda^\circ_{(H^+)}$ = 349.6 S cm^2 mol^{-1} and
$\lambda^\circ_{(HCOO^-)}$ = 54.6 S cm^2 mol^{-1}

23. (i) Why electrolysis of $NaBr_{(aq)}$ and $NaI_{(aq)}$ gives Br_2 and I_2 respectively while that of $NaF_{(aq)}$ gives O_2 instead of F_2?
(ii) (a) Why $\Lambda°_m$ for acetic acid cannot be determined experimentally?
(b) State Kohlrausch's law for electrical conductance of an electrolyte at infinite dilution.

24. (a) 19 g of molten $SnCl_2$ is electrolysed for some time using inert electrodes. 0.119 g of Sn is

deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the weights of $SnCl_2$: $SnCl_4$ after electrolysis. (At. wt. of Sn = 119)

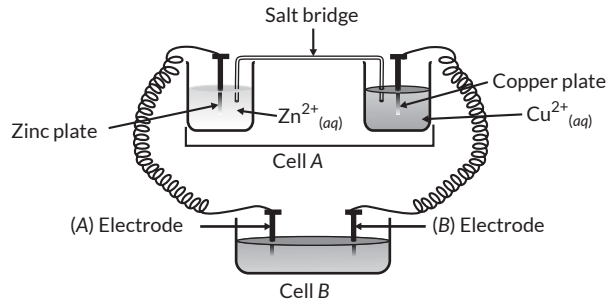
(b) A direct current deposits 19.58 g of potassium in one minute. How many grams of aluminium will be deposited by the same current in the same time? (At. wt. of K = 39, Al = 27)

25. (i) On passing equal amount of charge, 11.2 L of Cl_2 was liberated at STP from NaCl solution whereas 9.88 g of metal was deposited from a nitrate solution of this metal. If the specific heat of metal is 0.216 cal/g, what is the formula of metal nitrate?

(ii) A steady current was passed for 5 hours through two cells connected in series. First cell contains a solution of $AuCl_3$ and second contains $CuSO_4$ solution. 9.85 g of gold was deposited in the first cell. Find the amount of Cu deposited in the second cell. Also calculate the magnitude of current in ampere.

OR

Consider the figure and answer the following questions.



(i) Cell '*A*' has E_{cell} = 2 V and cell '*B*' has E_{cell} = 1.1 V which of the two cells '*A*' or '*B*' will act as an electrolytic cell? Which electrode reactions will occur in this cell?

(ii) If cell '*A*' has E_{cell} = 0.5 V and cell '*B*' has E_{cell} = 1.1 V then what will be the reactions at anode and cathode?

(iii) Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_{7(aq)}$, 0.20 M $Cr^{3+}_{(aq)}$ and 1.0×10^{-4} M $H^+_{(aq)}$. The half cell reaction is : $Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$ and the standard electrode potential is given as E° = 1.33 V.

Detailed SOLUTIONS

1. **(i) (b) :** $n_{NaCl} = \frac{4 \times 500}{1000} = 2\,mol$

$\therefore$ n_{Cl_2} = 1 mol

(ii) (b) : n_{Na} deposited = 2 mol

$\therefore$ n_{Na-Hg} formed = 2 mol

$\therefore$ Mass of amalgam formed = 2 × 223 = 446 g

(iii) (d): $2Na^+ + 2e^- \underset{(2F)}{\rightarrow} 2Na$

Total charge required = 2F = 2 × 96500 = 193000 C

(iv) (a)

(v) (a)

2. **(a):** Weak electrolytes dissociate partially in concentrated solution. On dilution, their degree of dissociation increases hence their Λ_m increases sharply.

3. **(a) :** Formation of oxygen has lower value of E^o than formation of chlorine even then it is not formed because it requires overvoltage.

4. **(b) :** Sulphuric acid being strong electrolyte undergoes complete ionization.

5. **(c) :** $\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{50}{250} \Rightarrow \alpha = 0.2 \times 100 = 20\%$

6. **(a):** The sulphuric acid concentration is maximum when the battery is fully charged.

7. **(a):** $E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Product]}{[Reactant]}$

$Cu \rightarrow Cu^{2+} + 2e^-$

$$E_{Cu/Cu^{2+}} = E^\circ_{Cu/Cu^{2+}} - \frac{0.059}{n} \log \frac{[Cu^{2+}]}{[Cu_{(s)}]}$$

$$= -0.34 - \frac{0.059}{2} \log \frac{[0.1]}{[Cu_{(s)}]}$$

$$= -0.34 - \frac{0.059}{2} \log(10^{-1}) = 0.34 + \frac{0.059}{2}$$

8. **(a):** More negative the value of reduction potential, stronger will be the reducing agent thus I^- is strongest reducing agent. More positive value of reduction potential shows good oxidising properties thus strongest oxidising agent is F_2.

9. Mg, Al, Zn, Fe, Cu

10. The salt bridge allows the movement of ions from one solution to the other without mixing of the two solutions. Moreover, it helps to maintain the electrical neutrality of the solutions in the two half cells.

11. At equilibrium, E_{cell} = 0 and $\Delta_r G$ = 0

OR

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

where, κ is the conductivity, *R* is resistance and *l*/*A* is the cell constant.

12. Under the conditions of electrolysis of aqueous sodium chloride, oxidation of water at anode requires overpotential hence Cl^- is oxidised instead of water.

13. Quantity of electricity passed
$Q = I \times t = 2.0\ A \times 3 \times 60 \times 60\ s = 21600\ C$

$$\underset{2\ F}{Hg^{2+} + 2e^-} \longrightarrow \underset{1\ mol}{Hg}$$

2×96500 C electricity produces 1 mole Hg

$$\therefore \quad 21600\ C \text{ will produce } = \frac{21600}{2 \times 96500}$$

$$= 0.112 \text{ mole of Hg}$$

14. Mercury cell : It is a miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices. In mercury cell the anode is zinc-mercury amalgam, and the cathode is a paste of mercury (II) oxide and carbon, electrolyte is a moist paste of KOH - ZnO.
The cell reactions are as follows :

Anode : $\underset{\text{(Amalgam)}}{Zn(Hg)} + 2OH^- \longrightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

Cathode : $HgO_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow Hg_{(l)} + 2OH^-$

Net reaction : $Zn(Hg) + HgO_{(s)} \longrightarrow ZnO_{(s)} + Hg_{(l)}$

The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its use.

OR

(i) In saline water the presence of Na^+ and Cl^- ions increases the conductivity of the liquid layer in contact with the metallic surface. This accelerates the formation of Fe^{2+} ions and hence that of rust $Fe_2O_3 \cdot xH_2O$.
(ii) Aluminium has a larger discharge potential than H^+ ions and thus during electrolysis of its aqueous solution. Al^{3+} ions are not discharged at cathode. Instead, H^+ ions are discharged at cathode to liberate H_2 gas.

15. Because in electrochemical series, standard reduction potential value of hydrogen is greater than the Zn but lower than the Cu.

16. Application of electrochemical series :
(i) Higher reduction potentials are strong oxidising agents while lower reduction potentials are strong reducing agents.
(ii) The electrode with higher electrode potential ($E°$) acts as cathode while with lower electrode potential will act as anode.
(iii) Predicting the feasibility of redox reaction.
(iv) Predicting the capability of metal to displace H_2 gas from acid.

17. The cell will be represented as
$Zn_{(s)} \mid Zn^{2+}_{(aq)} \| Ag^+_{(aq)} \mid Ag_{(s)}$
(i) Anode, *i.e.*, zinc electrode will be negatively charged.
(ii) Ions are the current carriers. The current will flow from silver to zinc in the external circuit.
(iii) At anode : $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
At cathode : $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

18. (a) Corrosion is the process of slowly eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, carbonates, etc. The corrosion of iron is called rusting.

Electrochemical theory of rusting of iron : According to electrochemical theory of rusting the impure iron surface behaves like small electrochemical cell. In this any point of iron acts as anode and other iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an electrolyte. The reactions are given below.

At anode : $Fe \rightarrow Fe^{2+} + 2e^-; E°_{Fe^{2+}/Fe} = -0.44\ V$

At cathode : $2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O; E°_{H^+/O_2/H_2O} = 1.23\ V$

Overall reaction : $Fe + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O;$
$E°_{cell} = 1.67\ V$

The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} ions, which form hydrated ferric oxide (rust).

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O \text{ (Rust)}$$

(b) Standard hydrogen electrode is the reference electrode whose electrode potential is taken as zero. The electrode potential of other electrode is measured with respect to it.

19. $C = 0.001$ M, $\kappa = 4 \times 10^{-5}$ S cm^{-1},
$\Lambda^\infty_m = 390$ S cm^2/mol

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

Substituting the values,

$$\Lambda_m = \frac{4 \times 10^{-5} \times 1000}{0.001} = 40 \text{ S cm}^2\text{/mol}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^\infty_m} = \frac{40}{390} = 0.10256\ ;\ 0.103$$

$$\underset{c(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{c\alpha}{CH_3COO^-} + \underset{c\alpha}{H^+}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.001(0.103)^2}{(1-0.103)} = \frac{1.061 \times 10^{-5}}{0.897} = 1.18 \times 10^{-5}$$

20. When the solution of a weak electrolyte is diluted, its degree of ionisation increases. There is an increase in the number of ions in the solution. Hence, the molar conductivity of a weak electrolyte increases on dilution.
Electrolytic conductivity, $\kappa = 3.72 \times 10^{-2}$ S cm^{-1}

Molar conductivity, $\Lambda_m = \frac{\kappa \times 10^3}{C}$

$$\Lambda_m = \frac{3.72 \times 10^{-2} \times 1000}{0.30} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

OR

(i) The alkaline medium prevents the availability of H^+ ions. This in turn reduces rate of oxidation of Fe to Fe^{2+}. Thus, the rusting of iron is inhibited.
(ii) Even if the zinc coating is broken in an iron pipe, the remaining zinc layer undergoes oxidation in preference to iron because it is more electropositive than iron. Hence, iron does not rust.

21. **(i)** $0.059 = \frac{+0.059}{2}\log\frac{0.001}{[M^{2+}]}$

$\log\frac{0.001}{[M^{2+}]} = 2$ or $[M^{2+}] = 10^{-5}$

Let solubility of salt be *s* mol/litre.

Thus, $MX_2 \longrightarrow \underset{s}{M^{2+}} + \underset{2s}{2X^-}$

$\therefore \quad K_{sp} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$

(ii) $\Delta G = -nFE_{cell} = -2 \times 96500 \times 0.059$

$= -11406.3 \text{ J mol}^{-1} \approx -11.4 \text{ kJ mol}^{-1}$

(iii) $OCl^- \longrightarrow Cl^-; E_1^\circ = 0.94 \text{ V}$

$Cl^- \longrightarrow 1/2Cl_2; E_2^\circ = -1.36 \text{ V}$

$OCl^- \longrightarrow 1/2Cl_2; E_3^\circ = ?$

Applying, $\Delta G^\circ = -nFE^\circ$

$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

$-n_3FE_3^\circ = -(n_1FE_1^\circ) + (-n_2FE_2^\circ)$

$n_1 = 2, \ n_2 = 1, n_3 = 1$

$-n_3E_3^\circ = -(n_1E_1^\circ + n_2E_2^\circ)$

$E_3^\circ = ((2 \times 0.94) - 1.36) \text{ V}$

$E_3^\circ = 0.52 \text{ V}$

OR

$Ag_{(s)} + Ag^+ (0.1 \text{ M}) \longrightarrow Ag^+ (\text{saturated } Ag_2CrO_4) + Ag_{(s)}$

$$E_{cell} = E_{cell}^\circ - \frac{0.059}{1}\log\frac{[Ag^+]_{\text{Satd. } Ag_2CrO_4}}{[Ag^+]}$$

$$0.164 = \frac{0.059}{1}\log\frac{0.1}{[Ag^+]_{\text{Satd. } Ag_2CrO_4}}$$

$[Ag^+]_{\text{satd. } Ag_2CrO_4} = 1.66 \times 10^{-4} \text{ M}$

So, $[CrO_4^{2-}] = \frac{1.66 \times 10^{-4}}{2}$

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp}(Ag_2CrO_4) = [Ag^+]^2 [CrO_4^{2-}]$

$$= (1.66 \times 10^{-4})^2 \left(\frac{1.66 \times 10^{-4}}{2}\right) = 2.287 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

22. (a) Water is a weak electrolyte, hence Λ_m° value of water is determined using Kohlrausch law.

$\Lambda_m^\circ (H_2O) \longrightarrow \lambda_m^\circ(H^+) + \lambda_m^\circ(OH^-)$

It can be determined by knowing the Λ_m° of three electrolytes HCl, NaOH and NaCl.

Applying Kohlrausch law,

$\Lambda_m^\circ(H_2O) \longrightarrow \Lambda_m^\circ(HCl) + \Lambda_m^\circ(NaOH) - \Lambda_m^\circ(NaCl)$

(b) Given, $\lambda_m^\circ(H^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$

$\lambda_m^\circ(HCOO^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$

$\Lambda_m^c(HCOOH) = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$

$\alpha = ?$

From Kohlrausch law,

$\Lambda_m^\circ(HCOOH) = \lambda_m^\circ(H^+) + \lambda_m^\circ(HCOO^-)$

or $\Lambda_m^\circ(HCOOH) = 349.6 \text{ S cm mol}^{-1} + 54.6 \text{ S cm}^2 \text{ mol}^{-1}$

$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$

Using formula

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{46.1 \text{ S cm}^2 \text{ mol}^{-1}}{404.2 \text{ S cm}^2 \text{ mol}^{-1}} = 0.114$$

Again, $K_a = \frac{\alpha^2 C}{1 - \alpha}$

$$= \frac{(0.114)^2 \times 0.025 \text{ mol L}^{-1}}{1 - 0.114} = 3.67 \times 10^{-4}$$

23. (i) Br^- and I^- ions have higher oxidation potentials than water. Hence, they are more easily oxidized. But F^- ions have lower oxidation potential than H_2O. So, H_2O is easily oxidized to give O_2 gas.

(ii) (a) Molar conductivity of weak electrolytes keeps on increasing with dilution and does not become constant even at very large dilutions. Therefore, Λ_m° for acetic acid cannot be determined experimentally.

(b) Kohlrausch's law states that at infinite dilution, when the dissociation of electrolyte is complete each ion makes a definite contribution towards the molar conductivity of electrolyte, irrespective of the nature of other ion with which it is associated.

$$\Lambda_m^\infty = \upsilon_+\lambda_+^\infty + \upsilon_-\lambda_-^\infty$$

24. (a) The reaction is :

$\underset{2 \times 190}{2SnCl_2} \longrightarrow \underset{261}{SnCl_4} + \underset{119}{Sn}$

119 g Sn is deposited from 380 g of $SnCl_2$

$\therefore$ 0.119 g Sn is deposited from $\frac{380}{119} \times 0.119$

$= 0.38 \text{ g of } SnCl_2$

Wt. of $SnCl_4$ formed = 0.38 – 0.119 = 0.261 g

Wt. of $SnCl_2$ left = 19 – 0.38 = 18.62 g

$\therefore$ Ratio of $SnCl_2 : SnCl_4 = 18.62 : 0.261$ or $= 71.34 : 1$

(b) Eq. wt. of K = $\frac{39}{1} = 39 \text{ g}$; Eq. wt. of Al $= \frac{27}{3} = 9 \text{ g}$

Also, $\frac{\text{wt. of Al deposited}}{\text{wt. of K deposited}} = \frac{\text{Eq. wt. of Al}}{\text{Eq. wt. of K}}$

Substituting values, $\frac{\text{wt. of Al } (W)}{19.58} = \frac{9}{39}$

$\Rightarrow W = \frac{9 \times 19.58}{39} = 4.52 \text{ g}$

Wt. of aluminium deposited = 4.52 g

25. (i) At. wt. of metal $= \frac{6.4}{\text{specific heat}} = \frac{6.4}{0.216} = 29.63$

Applying, $\frac{W}{W_{Cl_2}} = \frac{E_m}{E_{Cl_2}}$

Wt. of 22.4 L of Cl_2 at STP = 71 g

$\therefore$ Wt. of 11.2 L of Cl_2 at STP = $\frac{71}{22.4} \times 11.2 = 35.5 \text{g}$

Eq. wt. of $Cl_2 = \frac{71}{2} = 35.5 \text{ g}$

Eq. wt. of metal $= \frac{\text{At. wt.}}{\text{Valency}} = \frac{29.63}{n}$

Now, $\frac{9.88}{35.5} = \frac{\frac{29.63}{n}}{35.5}$

$n = \frac{29.63}{35.5} \times \frac{35.5}{9.88} = 2.99 \approx 3$ *i.e.*, Metal valency = 3

Hence, metal nitrate must be $M(NO_3)_3$.

(ii) Given : $W_1 = 9.85$ g Au from $AuCl_3$

$W_2 = ?$ for Cu from $CuSO_4$

$E_1 = \frac{197}{3}, E_2 = \frac{63.5}{2}$

Using formula, $\frac{W_1}{E_1}=\frac{W_2}{E_2}$

or $\frac{9.85}{197/3}=\frac{W_2}{63.5/2}$ or, $\frac{9.85\times3}{197}=\frac{W_2\times2}{63.5}$

or, $W_2=\frac{9.85\times3\times63.5}{197\times2}=4.76\text{ g}$

Again, 197 g Au requires 3 × 96500 C electricity

$\therefore$ 9.85 g Au requires $\frac{3\times96500\text{ C}}{197\text{ g}}\times9.85=14475\text{ C}$

Again, $Q = I \times t$

$\therefore \quad I=\frac{Q}{t}=\frac{14475}{5\times60\times60}=0.80\text{ A}$

OR

(i) Cell *B* will act as electrolytic cell as it has lower emf. The electrode reaction will be

$Zn^{2+} + 2e^- \rightarrow Zn$ (Cathode)

$Cu \rightarrow Cu^{2+} + 2e^-$ (Anode)

(ii) With the values of emf, cell *B* will act as galvanic cell due to higher emf and will push electrons into cell *A*. The electrode reactions will be

$Zn - 2e^- \rightarrow Zn^{2+}$ (Anode)

$Cu^{2+} + 2e^- \rightarrow Cu$ (Cathode)

(iii) For half cell reaction,

$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

$$E_{cell}=E^\circ_{cell}-\frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

Given, $E^\circ_{cell} = 1.33$ V, $n = 6$, $[Cr^{3+}] = 0.2$ M

$[Cr_2O_7^{2-}] = 0.1$ M, $[H^+] = 1 \times 10^{-4}$ M

$$\Rightarrow \quad E_{cell}=1.33\text{V}-\frac{0.0591}{6}\log\frac{(0.20)^2}{(0.1)(10^{-4})^{14}}$$

$$=1.33\text{V}-\frac{0.0591}{6}\log(4\times10^{55})$$

$$=1.33\text{ V}-\frac{0.0591}{6}[\log4+\log10^{55}]$$

$$=1.33\text{ V}-\frac{0.0591}{6}[\log4+55\log10]$$

$$=1.33\text{ V}-\frac{0.0591}{6}[0.602+55]$$

$$= 1.33\text{ V} - 0.548\text{ V} = 0.782\text{ V}$$

CHAPTER

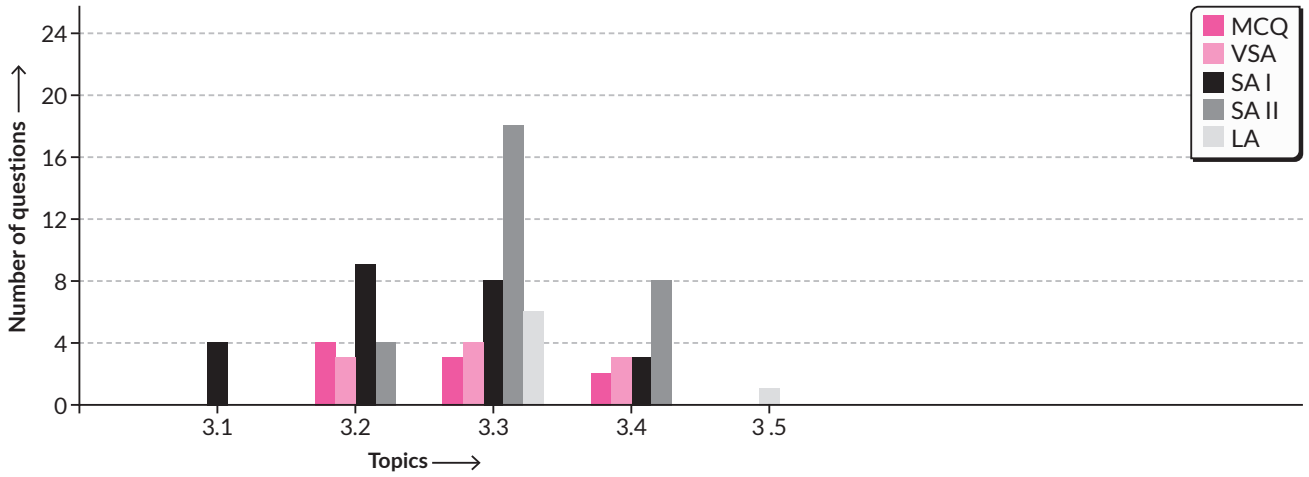
3

Chemical Kinetics

TOPICS

3.1 Rate of a Chemical Reaction
3.2 Factors Influencing Rate of a Reaction
3.3 Integrated Rate Equations
3.4 Temperature Dependence of the Rate of a Reaction
3.5 Collision Theory of Chemical Reactions

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topics 3.2 and 3.3 are highly scoring topics.
- Maximum total weightage is of Topic 3.3 *Integrated Rate Equations.*
- Maximum SA I type questions were asked from Topic 3.2 *Factors Influencing Rate of a Reaction.*
- Maximum VSA, SA II and LA type questions were asked from Topic 3.3 *Integrated Rate Equations.*

QUICK RECAP

- **Chemical kinetics :** It is the branch of chemistry which deals with the study of reaction rates and their mechanisms.
- **Rate of a reaction :** The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time. For the reaction,

  $R \longrightarrow P$, Rate $= -\frac{\Delta[R]}{\Delta t}$ or $+\frac{\Delta[P]}{\Delta t}$

- **Units of rate :** Concentration time^{-1} *i.e.*, mol L^{-1} s^{-1} or atm s^{-1} for gaseous reactions.
- **Average rate of reaction :** The rate of change in concentration of any reactant or product during a large time interval.

  $r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$

- **Instantaneous rate of reaction :** It is the rate of a reaction at a particular instant of time *i.e.*, when Δt approaches zero.

$$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$$

- **Factors influencing rate of a reaction :**
  - **Concentration :** Greater the concentrations of the reactants, faster is the rate of reaction.
  - **Physical state of reactants :** Reactions involving gaseous reactants are faster than reactions containing solid and liquid reactants.
  - **Temperature :** The rate of reaction increases with increase of temperature. For most of the reactions, rate of reaction becomes almost double with 10° C rise of temperature.
  - **Presence of catalyst :** A catalyst generally increases the speed of a reaction.
  - **Surface area of reactants :** For a reaction involving a solid reactant or catalyst, greater is the surface area, faster is the reaction.
  - **Presence of light :** Photochemical reactions take place in the presence of light only.
  - **Activation energy :** Lower the activation energy faster is the reaction.
- **Law of mass action and rate law :**

According to law of mass action, rate of reaction is proportional to the product of concentration of reactants, each concentration term raised to the power equal to stoichiometric coefficients.

$aA + bB \longrightarrow$ Product

Rate $\propto [A]^a[B]^b$ or Rate $= k[A]^a[B]^b$

where, k is a constant, known as **rate constant** or **velocity constant.** Experimentally, it was found that rate may not depend upon stoichiometric term 'a' concentration terms of A or stoichiometric term 'b' of B. Let rate of reaction depends upon 'α' concentration terms of A and 'β' concentration terms of B, experimentally.

Then, Rate $\propto [A]^{\alpha}[B]^{\beta}$ or Rate $= k[A]^{\alpha}[B]^{\beta}$

This expression is known as rate law which says that rate of reaction is proportional to product of concentration of reactants, each concentration term raised to the power on which rate of reaction actually depends.

Difference between rate law and law of mass action : Law of mass action is based on stoichiometry of a balanced chemical equation whereas rate law is based upon the concentration terms on which rate of reaction actually depends.

- **Order and molecularity :**

Molecularity of a reaction	Order of a reaction
It is the total number of species taking part in a chemical reaction.	It is the sum of the powers of the concentration terms of reacting species in the rate law equation.
It is a theoretical concept.	It is an experimental quantity.
It is derived from the mechanism of reaction.	It is derived from the rate expression.
It can neither be zero nor fractional. It is always a whole number.	It may be zero, fractional or an integer.
It is applicable only to elementary reactions. The overall molecularity of a complex reaction has no significance.	It is applicable to elementary as well as complex reactions.

- **Half life of a reaction :** The time in which the concentration of a reactant is reduced to one half of its initial concentration is called *half life of the reaction.*

$t_{1/2} \propto \frac{1}{a^{n-1}}$; where n is the order of the reaction.

Rate law, integrated rate law, half-life, unit of rate constant and graphical parameters for the reactions of different orders :

Order	Rate law	Integrated rate law	Half-life	Units of rate constant	Graphical parameters
0	Rate $= k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L^{-1} s^{-1}	$[A]_t$ *vs* t; slope $= -k$
1	Rate $= k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]_t$ *vs* t; slope $= -k$
2	Rate $= k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k[A]_0$	L mol^{-1} s^{-1}	$1/[A]_t$ *vs* t; slope $= k$
2	Rate $= k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	–	L mol^{-1} s^{-1}	–
n	Rate $= k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)[A]_0^{n-1}}$	$(mol\ L^{-1})^{1-n}$ s^{-1}	$\frac{1}{[A]^{n-1}}$ *vs* t; slope $= k$

Common examples of reaction of different order

- Zero order reactions
  (i) $H_{2(g)} + Cl_{2(g)} \xrightarrow{h\upsilon} 2HCl_{(g)}$
  (ii) $2NH_{3(g)} \xrightarrow{h\upsilon} N_{2(g)} + 3H_{2(g)}$
- First order reactions
  (i) $NH_4NO_2 \longrightarrow N_2 + 3H_2O$
  (ii) $2N_2O_5 \longrightarrow 4NO_2 + O_2$
- Second order reactions
  (i) $2HI \longrightarrow H_2 + I_2$
  (ii) $NO + O_3 \xrightarrow{h\upsilon} NO_2 + O_2$
- Third order reactions
  (i) $2NO + O_2 \longrightarrow 2NO_2$
  (ii) $2NO + Br_2 \longrightarrow 2NOBr$
- Fractional order reactions
  (i) $H_2 + Br_2 \longrightarrow 2HBr$
  Rate = $k[H_2][Br_2]^{1/2}$, Order = 1.5
  (ii) $CH_3CHO \longrightarrow CH_4 + CO$
  Rate = $k[CH_3CHO]^{3/2}$, Order = 1.5

Pseudo first order reactions : Those reactions which are not truly of the first order but under certain conditions become reactions of the first order are called *pseudo first order reactions. e.g.*,

- **Acid hydrolysis of ethyl acetate :**

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Rate = $k'[CH_3COOC_2H_5][H_2O]$
= $k[CH_3COOC_2H_5]$ where, $k = k'[H_2O]$

- **Acid catalysed inversion of cane sugar :**

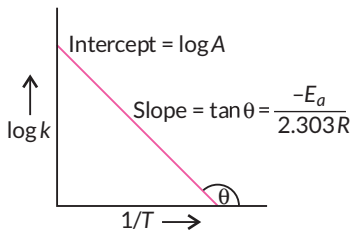
$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Cane sugar — Glucose — Fructose

Rate = $k[C_{12}H_{22}O_{11}]$

Effect of temperature on rate of reaction :

- For a chemical reaction with rise in temperature by 10° C, the rate constant is nearly doubled.
- **Arrhenius equation :** $k = Ae^{-E_a/RT}$

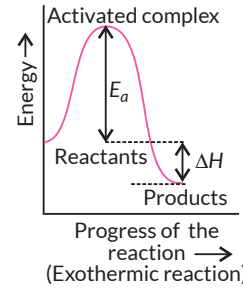
$$\log k = \log A - \frac{E_a}{2.303RT}$$

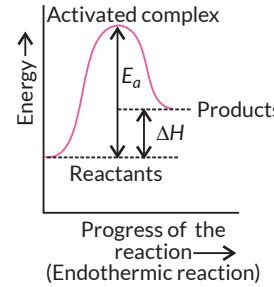


where, k = Rate constant,
A = Pre-exponential factor (frequency factor),
E_a = Activation energy, T = Temperature

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Activation energy : The minimum amount of energy required by reactant molecules to participate in a reaction is called *activation energy* (E_a).





- Activation energy = Threshold energy − Average kinetic energy of reacting molecules
- Activation energy (E_a) = $E_{(\text{activated complex})} - E_{(\text{ground state})}$
- ΔH = Activation energy of forward reaction − Activation energy of backward reaction

Collision theory of chemical reactions :

- Reaction occurs due to collision of molecules.
- All collisions are not effective.
- *Effective collisions* are those collisions in which molecules collide with sufficient kinetic energy (called *threshold energy* which is equal to activation energy + energy possessed by reacting species) and proper orientation.
- Rate = $PZ_{AB}e^{-E_a/RT}$ where, P = probability or steric factor which takes into account the fact that in a collision, molecules must be properly oriented and Z_{AB} = collision frequency (*i.e.*, the no. of collisions per second per unit volume of the reaction mixture) of reactants, A and B.

Chemical Kinetics

The branch of chemistry dealing with the study of rate of reaction, mechanism and factors affecting rate of reaction is known as chemical kinetics.

Rate of Reaction

It is defined as the change in concentration of any one of the reactants and products per unit time.

Average rate and instantaneous rate : The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.

Rate constant : It is equal to the rate of reaction when the concentration of each of the reactants is unity.

Units of rate constant :

n^{th} order reaction, $\frac{dx}{dt} = k(\text{conc.})^n$

$$k = \frac{dx}{dt} \times \frac{1}{(\text{conc.})^n}$$

$k = (\text{conc.})^{1-n}\ \text{time}^{-1}$

- For zero order reaction ($n = 0$), Unit of $k = \text{mol L}^{-1}\ \text{s}^{-1}$
- For 1st order reaction ($n = 1$), Unit of $k = \text{s}^{-1}$

Factors affecting rate of reaction:

- Concentration of reactants
- Medium
- Catalysts
- Surface area
- Effect of temperature

Order and Molecularity of Reaction

Order of reaction : It is defined as the sum of the powers of the concentration terms in the rate law.

For a given reaction,

$mA + nB \rightarrow$ Product

rate $= k[A]^x [B]^y$

$\therefore$ Order of reaction $= x + y$

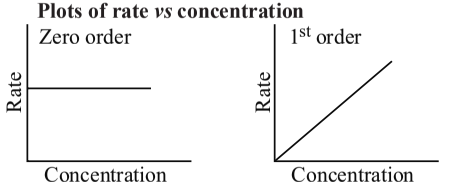
It can be zero order, first order and so on.

It can also be fractional.

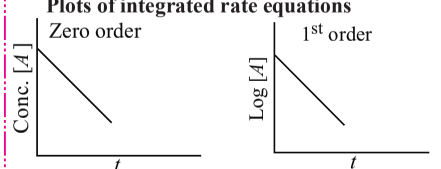
Molecularity of reaction : It is defined as the number of molecules of reactant taking part in a chemical reaction.

It can be 1, 2, 3... but can neither be zero nor fractional.

Plots of rate *vs* concentration



Plots of integrated rate equations



Integrated Rate Equation

For zero order: $k = \frac{1}{t}\{[A_0] - [A]\}$

For first order :

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

For n^{th} order :

$$k = \frac{1}{t(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

where

k = rate constant

$[A_0]$ = initial concentration

$[A]$ = final concentration

n = order of reaction

x = concentration of reactant decomposed in time t.

Half Life Period

Time in which the concentration of a reactant is reduced to half of its initial concentration.

- Half-life of n^{th} order reaction,

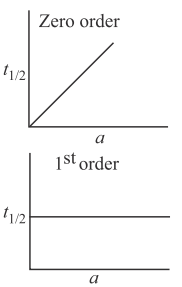
$$t_{1/2} = \frac{2^{n-1} - 1}{k_n (n-1) a^{n-1}}$$

or $t_{1/2} \propto \frac{1}{[a]^{n-1}}$

when $n \geq 2$

- Amount of substance left after n half-lives $= \frac{a}{2^n}$
- Average life, $t_{av} = 1.44 t_{1/2}$

- **Plots of half-lives *vs* initial concentration *a***



Temperature Dependence of Rate of Reaction

Collision theory :

$\therefore\ k = P Z e^{-E_a/RT}$

where

P = steric factor

Z = collision frequency

Concept of activation energy : The excess energy which must be supplied to the reactants to undergo chemical reactions is called activation energy (E_a).

$E_a = E(\text{threshold}) - E(\text{reactants})$

Arrhenius equation : Arrhenius proposed a quantitative relationship between rate constant and temperature as

$k = Ae^{-E_a/RT}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

or, $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$

- Plotting $\log k$ vs $\frac{1}{T}$,

slope $= -\frac{E_a}{2.303\ R}$

$\therefore\ E_a = -2.303\ R \times \text{slope}$

BRAIN MAP

Previous Years' CBSE Board Questions

3.1 Rate of a Chemical Reaction

SA I (2 marks)

1. In the given reaction, $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ the rate of formation of NH_3 is 3.6×10^{-4} mol L^{-1} s^{-1}.
   Calculate the
   (i) rate of reaction and
   (ii) rate of disappearance of $H_{2(g)}$.
   (Term-II, 2021-22) Ap

2. The following reaction was carried out in water :
   $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$
   The initial concentration of I^- was 0.30 M and the concentration after 10 minutes reduced to 0.28 M. Calculate the ratio of disappearance of I^- and production of I_2. *(2021 C)*

3. In the given reaction, $A + 3B \rightarrow 2C$, the rate of formation of C is 2.5×10^{-4} mol L^{-1} s^{-1}.
   Calculate the
   (i) rate of reaction, and
   (ii) rate of disappearance of B. *(2020)* U

4. For the reaction, $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$, the rate of formation of $NO_{2(g)}$ is 2.8×10^{-3} M s^{-1}. Calculate the rate of disappearance of $N_2O_{5(g)}$. *(2018)*

3.2 Factors Influencing Rate of a Reaction

MCQ

5. The following experimental rate data were obtained for a reaction carried out at 25°C:

$$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$$

Initial $[A_{(g)}]$ / mol dm^{-3}	Initial $[B_{(g)}]$/ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
3.0×10^{-2}	2.0×10^{-2}	1.89×10^{-4}
3.0×10^{-2}	4.0×10^{-2}	1.89×10^{-4}
6.0×10^{-2}	4.0×10^{-2}	7.56×10^{-4}

What are the orders with respect to $A_{(g)}$ and $B_{(g)}$?

	Order with respect to $A_{(g)}$	Order with respect to $B_{(g)}$
(a)	Zero	Second
(b)	First	Zero
(c)	Second	Zero
(d)	Second	First

(2023)

6. **Assertion (A) :** The molecularity of the reaction $H_2 + Br_2 \longrightarrow 2HBr$ appears to be 2.
   Reason (R) : Two molecules of the reactants are involved in the given elementary reaction.
   (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is true, but Reason (R) is false.
   (d) Assertion (A) is false, but Reason (R) is true.
   (2023)

7. **Assertion :** Order of reaction is applicable to elementary as well as complex reactions.
   Reason : For a complex reaction molecularity has no meaning.
   (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A)
   (b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A)
   (c) Assertion (A) is true, but Reason (R) is false.
   (d) Assertion (A) is false, but Reason (R) is true.
   (2023)

8. **Assertion (A) :** The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ appears to be 2.
   Reason (R) : Two molecules of the reactants are involved in the given elementary reaction.
   (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
   (d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

VSA (1 mark)

9. Calculate the overall order of the reaction whose rate law expression was predicted as :
   Rate = $k[NO]^{3/2}[O_2]^{1/2}$. *(2020)* U

10. Define the rate constant.
    (1/5, Foreign 2015, Delhi 2015C)

11. Define the specific rate of reaction. *(AI 2014C)* R

SA I (2 marks)

12. Define rate of reaction. Write two factors that affect the rate of reaction. *(Term-II, 2021-22, AI 2015)*

13. Write two differences between 'order of reaction' and 'molecularity of reaction'. *(Term-II, 2021-22C, Delhi 2014)*

14. For a reaction

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

the proposed mechanism is as given below :

(1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

(2) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

(i) Write rate law for the reaction.
(ii) Write the overall order of reaction.
(iii) Out of steps (1) and (2), which one is rate determining step? *(Delhi 2019)* Ap

15. For a reaction : $2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$; Rate = k
(i) Write the order and molecularity of this reaction.
(ii) Write the unit of k. *(Delhi 2016)*

16. For a reaction : $H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$; Rate = k
(i) Write the order and molecularity of this reaction
(ii) Write the unit of k. *(AI 2016)*

17. For a reaction $A + B \rightarrow P$, the rate is given by Rate = $k[A][B]^2$
(i) How is the rate of reaction affected if the concentration of B is doubled?
(ii) What is the overall order of reaction if A is present in large excess? *(2/5, Delhi 2015)*

18. Write units of rate constants for zero order and for the second order reactions if the concentration is expressed in mol L^{-1} and time in second. *(AI 2015C)*

19. (i) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction?
(ii) Write the unit of rate constant 'k' for the first order reaction. *(Delhi 2014C)* U

20. A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half ? *(AI 2014C)*

SA II (3 marks)

21. Following data were obtained for the given reaction : $X + Y \longrightarrow$ Product

Exp.	[X]/M	[Y]/M	Initial Rate M min^{-1}
1	0.1 M	0.2 M	0.05
2	0.2 M	0.2 M	0.10
3	0.1 M	0.1 M	0.05

(i) Find the order of reaction with respect to X and Y.
(ii) Write the rate law expression.
(iii) Find the rate constant. *(2021C)* Ev

22. How will the rate of the reaction be affected when
(a) surface area of the reactant is reduced,
(b) catalyst is added in a reversible reaction, and
(c) temperature of the reaction is increased? *(2020)*

23. The following data were obtained for the reaction : $A + 2B \longrightarrow C$

Experiment	[A]/M	[B]/M	Initial rate of formation of C/M min^{-1}
1	0.2	0.3	4.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.4	0.3	1.68×10^{-1}
4	0.1	0.4	2.40×10^{-2}

(a) Find the order of reaction with respect to A and B.
(b) Write the rate law and overall order of reaction.
(c) Calculate the rate constant (k). *(2019)* An

24. A reaction is second order in A and first order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of A three times?
(iii) How is the rate affected when the concentration of both A and B are doubled? *(2018 C)*

3.3 Integrated Rate Equations

MCQ

25. The order of the reaction

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\upsilon} 2HCl_{(g)} \text{ is}$$

(a) 2 (b) 1 (c) 0 (d) 3 *(2023)*

26. The half-life period for a zero order reaction is equal to

(a) $\frac{0.693}{k}$ (b) $\frac{2k}{[R]_0}$ (c) $\frac{2.303}{k}$ (d) $\frac{[R]_0}{2k}$

(where $[R]_0$ is initial concentration of reactant and k is rate constant.) *(2020)* An

27. **Assertion (A) :** Hydrolysis of an ester follows first order kinetics.
Reason (R) : Concentration of water remains nearly constant during the course of the reaction.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

VSA (1 mark)

28. For a reaction $R \rightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?
(Term-II, 2021-22, Delhi 2017)

29. Write the slope value obtained in the plot of ln[R] *vs.* time for a first order reaction. *(One word, 2020)*

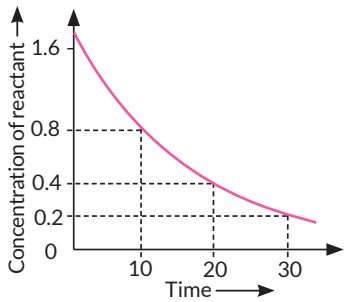
30. Write the slope value obtained in the plot of log $[R_o]$ / $[R]$ vs. time for a first order reaction.
(2020) An

31. Define the following term :
Pseudo first order reaction
(NCERT Exemplar, 1/2, Delhi 2014)

SA I (2 marks)

32. Answer the following questions (Do any two) :
(a) Identify the order of reaction from the following unit for its rate constant : L mol^{-1} s^{-1}
(b) The conversion of molecules *A* to *B* follow second order kinetics. If concentration of *A* is increased to three times, how will it affect the rate of formation of *B*?
(c) Write the expression of integrated rate equation for zero order reaction.
(Term II, 2021-22) U

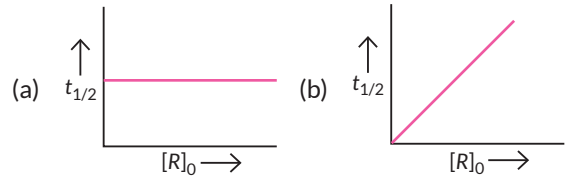
33. Analyse the given graph, drawn between concentration of reactant *vs.* time.



(a) Predict the order of reaction.
(b) Theoretically, can the concentration of the reactant reduce to zero after infinite time. Explain. *(2020)* Ev

34. Define rate constant and give the mathematical relation between rate constant and half-life period for a first order reaction. *(2020C)* R

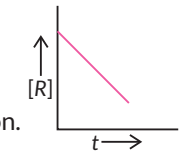
35. Define order of reaction. Predict the order of reaction in the given graphs :



where $[R]_0$ is the initial concentration of reactant and $t_{1/2}$ is half-life. *(2019)* Ev

36. For a reaction, $C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}$,
rate = 5.5×10^{-14} $[C_2H_4]$.
(a) Write the unit of rate constant.
(b) Calculate its half-life ($t_{1/2}$). *(2019 C)*

37. For a chemical reaction $R \rightarrow P$, the variation in the concentration $[R]$ *vs.* time (t) plot is given as



(i) Predict the order of the reaction.
(ii) What is the slope of the curve?
(2/5, AI 2019, AI 2014)

38. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
(NCERT, AI 2017C)

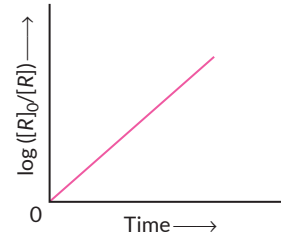
39. Define half-life of a reaction. Write the expression of half-life for
(i) zero order reaction and
(ii) first order reaction. *(Foreign 2014)*

SA II (3 marks)

40. (a) For the reaction
$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$ at 318 K
Calculate the rate of reaction if rate of disappearance of $N_2O_{5(g)}$ is 1.4×10^{-3} M s^{-1}.
(b) For a first order reaction derive the relationship $t_{99\%} = 2t_{90\%}$ *(2023)*

41. A first order reduction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.
Given : [log 2 = 0.3, log 3 = 0.48, log 4 = 0.6, log 5 = 0.7]
(Term-II, 2021-22) Ap

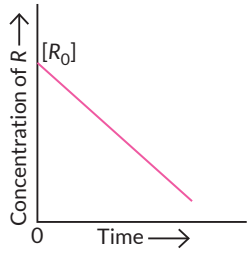
42. Observe the graph shown in figure and answer the following questions :



(a) What is the order of the reaction?
(b) What is the slope of the curve?
(c) Write the relationship between *k* and $t_{1/2}$ (half life period). *(Term II, 2021-22)* Ap

43. A first order reaction is 50% complete in 40 minutes. Calculate the time required for the completion of 90% of reaction.
[Given : log 2 = 0.3010, log 10 = 1]
(Term-II, 2021-22)

44. The variation in the concentration (*R*) *vs.* time (*t*) plot is given below. Answer the following questions on the basis of the given figure :



(i) Predict the order of the reaction.
(ii) What is the slope of the curve?
(iii) What are the units of the rate constant *k*?
(Term-II, 2021-22C) Ev

45. A first order reaction has a rate constant $4.9 \times 10^{-3}\ s^{-1}$. How long will 4 g of this reactant take to reduce to 3 g ? [log 4 = 0.6020, log 3 = 0.4771] *(2020C)*

46. A first order reaction is 40% complete in 80 minutes. Calculate the value of rate constant (*k*). In what time will the reaction be 90% completed?
[Given : log 2 = 0.3010, log 3 = 0.4771,
log 4 = 0.6021, log 5 = 0.6771, log 6 = 0.7782]
(2020)

47. The decomposition of NH_3 on platinum surface is zero order reaction. If rate constant (*k*) is $4 \times 10^{-3}\ M\ s^{-1}$, how long will it take to reduce the initial concentration of NH_3 from 0.1 M to 0.064 M?
(Delhi 2019)

48. A first order reaction takes 30 minutes for 20% decomposition. Calculate $t_{1/2}$.
[log 2 = 0.3010] *(3/5, AI 2019)*

49. Following data are obtained for the reaction :

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2} O_2$$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.
(b) Calculate the half-life.
(Given : log 2 = 0.3010, log 4 = 0.6021)
(Delhi 2017) An

50. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.
(Given : log 2 = 0.3010, log 3 = 0.4771,
log 4 = 0.6021) *(AI 2017)* An

51. For the first order thermal decomposition reaction, the following data were obtained :
$C_2H_5Cl_{(g)} \rightarrow C_2H_{4(g)} + HCl_{(g)}$

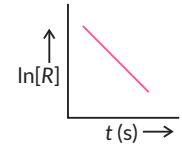
Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant.
(Given : log 2 = 0.301, log 3 = 0.4771,
log 4 = 0.6021) *(AI 2016)*

52. A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. (log 2 = 0.3010)
(3/5, Delhi 2015) An

53. A first order reaction takes 10 minutes for 25% decomposition. Calculate $t_{1/2}$ for the reaction.
(Given : log 2 = 0.3010, log 3 = 0.4771,
log 4 = 0.6021) *(3/5, Foreign 2015)*

54. For a chemical reaction $R \longrightarrow P$, the variation in the concentration, ln [*R*] *vs.* time (s) plot is given as



(i) Predict the order of the reaction.
(ii) What is the slope of the curve?
(iii) Write the unit of the rate constant for this reaction. *(3/5, Foreign 2015)*

55. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its $1/10^{th}$ value? *(AI 2015C)*

56. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume :

$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$

Experiment	Time/s	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.
(Given : log 4 = 0.6021, log 2 = 0.3010)
(Delhi, AI, Foreign 2014) Ev

57. Hydrogen peroxide, $H_2O_{2(aq)}$ decomposes to $H_2O_{(l)}$ and $O_{2(g)}$ in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3}\ min^{-1}$.
(i) How long will it take for 15% of a sample of H_2O_2 to decompose?
(ii) How long will it take for 85% of the sample to decompose? *(Delhi 2014C)* Ev

LA (4/5 marks)

The following questions are case based questions. Read the case carefully and answer the questions that follow.

58. The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. Mathematical representation of rate of reaction is given by rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation.

(i) What is average rate of reaction?

(ii) Write two factors that affect the rate of reaction.

(iii) (1) What happens to rate of reaction for zero order reaction?

(2) What is the unit of k for zero order reaction?

OR

(iii) (1) For a reaction $P + 2Q \longrightarrow$ Products
Rate = $k[P]^{1/2}[Q]^{1}$. What is the order of the reaction?

(2) Define pseudo first order reaction with an example. *(2023)*

59. Read the passage given below and answer the questions that follow :

The rate law for a chemical reaction relates the reaction rate with the concentrations or partial pressures of the reactants. For a general reaction, $aA + bB \rightarrow C$, with no intermediate steps in its reaction mechanism, meaning that it is an elementary reaction, the rate law is given by $r = k[A]^x[B]^y$, where $[A]$ and $[B]$ express the concentrations of A and B in moles per litre. Exponents x and y vary for each reaction and are determined experimentally. The value of k varies with conditions that affect reaction rate, such as temperature, pressure, surface area, etc. The sum of these exponents is known as overall reaction order. A zero order reactions has constant rate that is independent of the concentration of the reactions. A first order reaction depends on the concentration of only one reactant. A reaction is said to be second order when the overall order is two. Once we have determined the order of the reaction, we can go back and plug in one set of our initial values and solve for k.

(i) Calculate the overall order of a reaction which has the following rate expression :
Rate = $k\,[A]^{1/2}\,[B]^{3/2}$

(ii) What is the effect of temperature on rate of reaction?

(iii) What is meant by rate of a reaction?

(iv) (a) A first order reaction takes 77.78 minutes for 50% completion. Calculate the time required for 30% completion of this reaction. (log 10 = 1, log 7 = 0.8450)

OR

(b) A first order reaction has a rate constant 1×10^{-3} per sec. How long will 5 g of this reactant take to reduce to 3 g?
(log 3 = 0.4771 ; log 5 = 0.6990)
(Term II, 2021-22) Ev

60. Read the following passage and answer the questions that follow :

The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law :

Rate = $k[A]^x\,[B]^y$

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of $x + y$ gives the overall order of a reaction.

When a sequence of elementary reactions gives us the products, the reactions are called complex reactions. Molecularity and order of an elementary reaction are same. Zero order reaction are relatively uncommon but they occur under special conditions. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

(a) What is the effect of temperature on the rate constant of a reaction?

(b) For a reaction $A + B \rightarrow$ Product, the rate law is given by, Rate = $k[A]^2[B]^{1/2}$. What is the order of the reaction?

(c) How order and molecularity are different for complex reactions?

(d) A first order reaction has a rate constant $2 \times 10^{-3}\ s^{-1}$. How long will 6 g of this reactant take to reduce to 2 g?

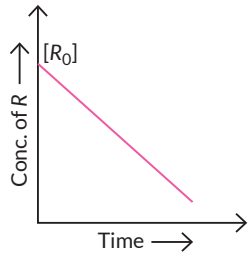
OR

The half life for radioactive decay of ^{14}C is 6930 years. An archaeological artifact containing wood had only 75% of the ^{14}C found in a living tree. Find the age of the sample.
[log 4 = 0.6021; log 3 = 0.4771; log 2 = 0.3010; log 10 = 1] *(Term II, 2021-22)* Cr

61. (a) A first order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% completed ?

(b) Define order of reaction. Write the condition under which a bimolecular reaction follows first order kinetics. *(2020)* U

62. (a) Visha plotted a graph between concentration of R and time for a reaction $R \rightarrow P$. On the basis of this graph, answer the following questions :



(i) Predict the order of reaction.
(ii) What does the slope of the line indicate?
(iii) What are the units of rate constant?

(b) A first order reaction takes 25 minutes for 25% decomposition. Calculate $t_{1/2}$.
[Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021] *(2020)*

63. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

t/s	0	30	60
$[CH_3COOCH_3]$/mol L^{-1}	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.
(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(Given : log 2 = 0.3010, log 4 = 0.6021)
(Delhi 2015)

3.4 Temperature Dependence of the Rate of a Reaction

MCQ

64. Which of the following is affected by catalyst?
(a) ΔH (b) ΔG (c) E_a (d) ΔS
(2023)

65. A biochemical reaction was carried out in the absence of enzyme and the rate of reaction was found to be 10^{-6} min^{-1}. If the same reaction is now carried out in the presence of enzyme, then the E_a for the reaction will be
(a) same
(b) greater than 10^{-6} min^{-1}
(c) lower than 10^{-6} min^{-1}
(d) data insufficient, E_a cannot be predicted.
(2020C) U

VSA (1 mark)

66. Will the rate constant of the reaction depend upon T if the E_{act} (activation energy) of the reaction is zero?
(One word, 2020)

67. What is the effect of adding a catalyst on
(a) activation energy (E_a), and
(b) Gibbs energy (ΔG) of a reaction? *(AI 2017)* Ap

68. Define the following :
Energy of activation of reaction.
(1/5, Foreign 2015, AI 2014C)

SA I (2 marks)

69. What happens to the rate constant k and activation energy E_a as the temperature of a chemical reaction is increased? Justify. *(2023)*

70. Draw the plot of ln k *vs* $1/T$ for a chemical reaction. What does the intercept represent? What is the relation between slope and E_a? *(2/5, AI 2019)*

71. How does a change in temperature affect the rate of a reaction? How can this effect on the rate constant of reaction be represented quantitatively? *(AI 2014C)*

SA II (3 marks)

72. The rate constant for the first order decomposition of N_2O_5 is given by the following equation :
$k = (2.5 \times 10^{14}\ s^{-1})\ e^{(-25000\ K)/T}$
Calculate E_a for this reaction and rate constant if its half-life period be 300 minutes. *(2020)* Ap

73. The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.
[R = 8.314 J K^{-1} mol^{-1}, log 4 = 0.6021]
(NCERT, 3/5, AI 2019)

74. The rate constant of a first order reaction increases from 2×10^{-2} to 6×10^{-2} when the temperature changes from 300 K to 320 K. Calculate the energy of activation.
(Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)
(2019 C)

75. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction. (Given : log 2 = 0.3010, log 4 = 0.6021, R = 8.314 J K^{-1} mol^{-1}) *(2018)*

76. The rate constant for the first order decomposition of H_2O_2 is given by the following equation :

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} K$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.
(Given : R = 8.314 J K^{-1} mol^{-1}) *(Delhi 2016)* An

77. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a). (log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021) *(Delhi 2015)*

78. The rate constants of reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of activation energy, E_a (R = 8.314 J K^{-1} mol^{-1}). *(Delhi 2015C)*

79. For a decomposition reaction, the values of k at two different temperatures are given below:
$k_1 = 2.15 \times 10^{-8}$ L/(mol.s) at 650 K
$k_2 = 2.39 \times 10^{-8}$ L/(mol.s) at 700 K
Calculate the value of E_a for the reaction.
(R = 8.314 J K^{-1} mol^{-1}) *(AI 2014C)*

3.5 Collision Theory of Chemical Reactions

80. (a) The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its $\frac{1}{16}$ th value?
(b) Write two factors that affect the rate of a chemical reaction.
(c) Write two conditions for the collisions to be effective collisions. *(2020)*

CBSE Sample Questions

3.2 Factors Influencing Rate of a Reaction

MCQ

1. For the reaction, $A + 2B \rightarrow AB_2$, the order w.r.t. reactant A is 2 and w.r.t. reactant B is zero. What will be change in rate of reaction if the concentration of A is doubled and B is halved?
(a) Increases four times
(b) Decreases four times
(c) Increases two times
(d) No change *(2022-23)*

SA I (2 marks)

2. Explain how and why will the rate of reaction for a given reaction be affected when
(a) a catalyst is added
(b) the temperature at which the reaction was taking place is decreased? *(2022-23)*

3. For a reaction the rate law expression is represented as follows :
Rate = $k\,[A][B]^{1/2}$
(i) Interpret whether the reaction is elementary or complex. Give reason to support your answer.
(ii) Write the units of rate constant for this reaction if concentration of A and B is expressed in moles/L. *(2020-21)* Ap

4. The following results have been obtained during the kinetic studies of the reaction :
$P + 2Q \rightarrow R + 2S$

Exp.	Initial P (mol/L)	Initial Q (mol/L)	Initial Rate of Formation of R (M min^{-1})
1.	0.10	0.10	3.0×10^{-4}
2.	0.30	0.30	9.0×10^{-4}
3.	0.10	0.30	3.0×10^{-4}
4.	0.20	0.40	6.0×10^{-4}

Determine the rate law expression for the reaction.
(2020-21) Ev

3.3 Integrated Rate Equations

MCQ

5. Which radioactive isotope would have the longer half-life ^{15}O or ^{19}O? (Given rate constants for ^{15}O and ^{19}O are 5.63×10^{-3} s^{-1} and $k = 2.38 \times 10^{-2}$ s^{-1} respectively.)
(a) ^{15}O
(b) ^{19}O
(c) Both will have the same half-life
(d) None of the above, information given is insufficient *(2022-23)*

SA I (2 marks)

6. A first-order reaction takes 69.3 min for 50% completion. What is the time needed for 80% of the reaction to get completed?
(Given : log 5 = 0.6990, log 8 = 0.9030, log 2 = 0.3010)
(2022-23)

7. The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees.

How old is that piece of wood? (log 3 = 0.4771, log 7 = 0.8540 , Half-life of C-14 = 5730 years)

(2020-21)

LA (5 marks)

8. **Read the passage given below and answer the questions that follow.**

Are these nuclear reactions going on in our bodies?

There are nuclear reactions constantly occurring in our bodies, but there are very few of them compared to the chemical reactions, and they do not affect our bodies much. All of the physical processes that take place to keep a human body running are chemical processes. Nuclear reactions can lead to chemical damage, which the body may notice and try to fix.

The nuclear reaction occurring in our bodies is radioactive decay. This is the change of a less stable nucleus to a more stable nucleus. Every atom has either a stable nucleus or an unstable nucleus, depending on how big it is and on the ratio of protons to neutrons. The ratio of neutrons to protons in a stable nucleus is thus around 1:1 for small nuclei ($Z < 20$). Nuclei with too many neutrons, too few neutrons, or that are simply too big are unstable. They eventually transform to a stable form through radioactive decay. Wherever there are atoms with unstable nuclei (radioactive atoms), there are nuclear reactions occurring naturally. The interesting thing is that there are small amounts of radioactive atoms everywhere: in your chair, in the ground, in the food you eat, and yes, in your body.

The most common natural radioactive isotopes in humans are carbon-14 and potassium-40. Chemically, these isotopes behave exactly like stable carbon and potassium. For this reason, the body uses carbon-14 and potassium-40 just like it does normal carbon and potassium; building them into the different parts of the cells, without knowing that they are radioactive. In time, carbon-14 atoms decay to stable nitrogen atoms and potassium-40 atoms decay to stable calcium atoms. Chemicals in the body that relied on having a carbon-14 atom or potassium-40 atom in a certain spot will suddenly have a nitrogen or calcium atom. Such a change damages the chemical. Normally, such changes are so rare, that the body can repair the damage or filter away the damaged chemicals.

The natural occurrence of carbon-14 decay in the body is the core principle behind carbon dating. As long as a person is alive and still eating, every carbon-14 atom that decays into a nitrogen atom is replaced on average with a new carbon-14 atom. But once a person dies, he stops replacing the decaying carbon-14 atoms. Slowly the carbon-14 atoms decay to nitrogen without being replaced, so that there is less and less carbon-14 in a dead body. The rate at which carbon-14 decays is constant and follows first order kinetics. It has a half - life of nearly 6000 years, so by measuring the relative amount of carbon-14 in a bone, archeologists can calculate when the person died. All living organisms consume carbon, so carbon dating can be used to date any living organism, and any object made from a living organism. Bones, wood, leather, and even paper can be accurately dated, as long as they first existed within the last 60,000 years. This is all because of the fact that nuclear reactions naturally occur in living organisms.

(*Source: The textbook Chemistry: The Practical Science by Paul B. Kelter, Michael D. Mosher and Andrew Scott states*)

(a) Why is carbon -14 radioactive while carbon-12 not? (Atomic number of carbon: 6)

(b) Researchers have uncovered the youngest known dinosaur bone, dating around 65 million years ago. How was the age of this fossil estimated?

(c) Which are the two most common radioactive decays happening in human body?

(d) Suppose an organism has 20 g of carbon-14 at its time of death. Approximately how much carbon-14 remains after 10,320 years? (Given antilog 0.517 = 3.289)

OR

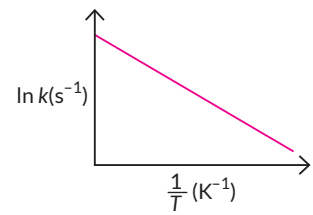
Approximately how old is a fossil with 12 g of carbon-14 if it initially possessed 32 g of carbon-14? (Given log 2.667 = 0.4260)

(Term II, 2021-22)

3.4 Temperature Dependence of the Rate of a Reaction

MCQ

9. Arrhenius equation can be represented graphically as follows :



The (i) intercept and (ii) slope of the graph are

(a) (i) ln A (ii) E_a/R (b) (i) A (ii) E_a

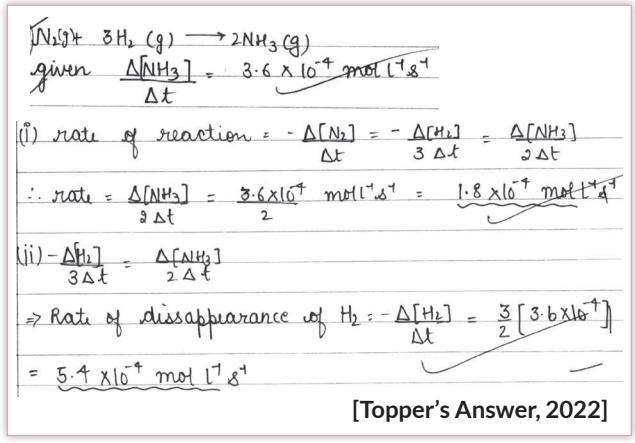
(c) (i) ln A (ii) $-E_a/R$ (d) (i) A (ii) $-E_a$

(2022-23)

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1.


$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
given $\frac{\Delta[NH_3]}{\Delta t} = 3.6 \times 10^{-4}$ mol $l^{-1} s^{-1}$
(i) rate of reaction $= -\frac{\Delta[N_2]}{\Delta t} = -\frac{\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t}$
$\therefore$ rate $= \frac{\Delta[NH_3]}{2\Delta t} = \frac{3.6\times10^{-4}}{2}$ mol $l^{-1} s^{-1} = 1.8 \times 10^{-4}$ mol $l^{-1} s^{-1}$
(ii) $-\frac{\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t}$
$\Rightarrow$ Rate of disappearance of $H_2 = -\frac{\Delta[H_2]}{\Delta t} = \frac{3}{2}[3.6\times10^{-4}]$
$= 5.4 \times 10^{-4}$ mol $l^{-1} s^{-1}$

[Topper's Answer, 2022]

2. $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

According to rate law expression

$$-\frac{d[Br_2]}{dt} = -\frac{1}{2}\frac{d[I^-]}{dt} = +\frac{1}{2}\frac{d[Br^-]}{dt} = +\frac{d[I_2]}{dt}$$

$$-\frac{d[I_2]}{dt} = \frac{0.30 - 0.28}{10} = 0.002 \text{ M min}^{-1}$$

Now, $-\frac{1}{2}\frac{d[I^-]}{dt} = +\frac{d[I_2]}{dt}$

or $\frac{d[I_2]}{dt} = \frac{1}{2} \times 0.002 \text{ M min}^{-1} = 0.001 \text{ M min}^{-1}$

Ratio of disappearance of I^- and production of I_2 = $\frac{0.002}{0.001} = \frac{2}{1}$ i.e., 2 : 1.

3. Given, $\frac{d[C]}{dt} = 2.5 \times 10^{-4}$ mol $L^{-1} s^{-1}$

According to rate law expression,

$$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

(i) Rate of reaction $= \frac{1}{2}\frac{d[C]}{dt}$

$= \frac{1}{2} \times 2.5 \times 10^{-4}$ mol $L^{-1} s^{-1} = 1.25 \times 10^{-4}$ mol $L^{-1} s^{-1}$

(ii) Rate of disappearance of $B = -\frac{d[B]}{dt} = \frac{3}{2}\frac{d[C]}{dt}$

$= \frac{3}{2} \times 2.5 \times 10^{-4}$ mol $L^{-1} s^{-1} = 3.75 \times 10^{-4}$ mol $L^{-1} s^{-1}$

Concept Applied

➲ For expressing the rate of a reaction where stoichiometric coefficients of reactants and products are not equal to one, the rate of disappearance or appearance is divided by the respective stoichiometric coefficients.

4. Given, $\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3}$ M s^{-1}

According to rate law expression,

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\therefore \quad -\frac{d[N_2O_5]}{dt} = \frac{2}{4} \times 2.8 \times 10^{-3}$$

$$\frac{-d[N_2O_5]}{dt} = \frac{1}{2} \times 2.8 \times 10^{-3} = 1.4 \times 10^{-3} \text{ M s}^{-1}$$

5. **(c):** Rate $= k[A]^x [B]^y$

From exp (1), $1{\cdot}89 \times 10^{-4} = k(3{\cdot}0 \times 10^{-2})^x (2{\cdot}0 \times 10^{-2})^y$ ...(i)

From exp (2), $1{\cdot}89 \times 10^{-4} = k (3.0 \times 10^{-2})^x (4{\cdot}0 \times 10^{-2})^y$...(ii)

Dividing (ii) by (i), we get $1 = (2)^y$

$\therefore \boxed{y = 0}$

From exp (3),

$7{\cdot}56 \times 10^{-4} = k(6{\cdot}0 \times 10^{-2})^x (4{\cdot}0 \times 10^{-2})^y$ ...(iii)

Dividing (iii) by (ii), we get

$$\frac{7{\cdot}56\times10^{-4}}{1{\cdot}89\times10^{-4}} = \frac{(6{\cdot}0\times10^{-2})^x}{(3.0\times10^{-2})^x}$$

$4 = (2)^x$

$(2)^2 = (2)^x$

$\boxed{x = 2}$

Rate $= k[A]^2 [B]^0$

6. **(a):** The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called the molecularity of a reaction. Thus, for the reaction, $H_2 + Br_2 \longrightarrow 2HBr$, the molecularity will be 2 as two molecules of reactants are involved in elementary reaction.

7. **(b):** Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction, molecularity has no meaning.

8. **(a):** Molecularity is two because two molecules of the reactants are involved in the given elementary reaction.

9. Given, rate $= k[NO]^{3/2} [O_2]^{1/2}$

$\therefore$ Overall order $= \frac{3}{2} + \frac{1}{2} = \frac{4}{2} = 2$

10. Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

11. At a given temperature, rate is equal to the rate constant of reaction when concentration of the reactant

in unity. Thus rate constant is also known as specific reaction rate.
In the case of two reactants, the reaction may be written as :

$A + B \rightarrow$ Products

$$r = \frac{dx}{dt} = k\,C_A C_B$$

where all the terms have their usual meaning.
If $C_A = C_B = 1$ then $r = k$.

12. Change in concentration (*i.e.*, either decrease in concentration of reactant or increase in concentration of product) per unit time is called rate of reaction.

Following factors affect the rate of a chemical reaction :
(i) Concentration of reactants : Higher the concentration of reactants, faster would be the rate of reaction.
Rate = $k\,C^n$, where C = concentration of reactant.
(ii) Temperature : The rate of reaction increases with the temperature. For every 10°C rise in temperature rate of reaction increases 2 to 3 times.

13. Differences between order and molecularity of a reaction are the following :

	Order of a reaction	Molecularity of a reaction
1.	It is the sum of powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2.	It can be zero or even a fraction.	It is always a whole number.

Key Points

- Generally, in a complex reaction the order of reaction is equal to the molecularity of the slowest step.

14. (i) Rate = $k[H_2O_2][I^-]$
(ii) Overall order of reaction is 2.
(iii) Step (1) being the slow step is the rate determining step of the reaction.

Concept Applied

- Slowest step of the mechanism is always the rate determining step.

15. (i) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.
In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.
However, two molecules of ammonia react to give products thus, the molecularity is two.
(ii) For a zero order reaction, unit of rate constant is mol L^{-1} s^{-1}.

16. (i) Experimentally, it is found that the rate of reaction is independent of the concentration of H_2 and Cl_2. Hence, it is a zero order reaction.
Molecularity = 2
(ii) Unit of k = mole $litre^{-1}$ sec^{-1}

Concept Applied

- Rate = $k[\text{conc}]^n$

$$k = \frac{\text{Rate}}{[\text{Conc}]^n} \Rightarrow \text{unit of } k = \frac{\text{Mol L}^{-1}\text{ s}^{-1}}{[\text{Mol L}^{-1}]^n}$$

Where n = order of reaction.

17. (i) From the rate law equation, order of reaction w.r.t. B is 2. Hence, if concentration of B is doubled, rate will become four times.
(ii) If A is present in large excess, rate of reaction will be independent of concentration of A and hence, order of reaction will be 2.

18. Unit of rate constant (k), for zero order reaction.
Rate = $k[A]^0 \Rightarrow k$ = mol L^{-1} s^{-1}
Unit of rate constant (k), for second order reaction
Rate = $k[A]^2 \Rightarrow k$ = L mol^{-1} s^{-1}

19. (i) Order of reaction is sum of powers of concentration terms,
$\therefore$ Order of reaction = 1 + 2 = 3
(ii) Unit of rate constant for first order reaction is s^{-1}.

20. Let the concentration of the reactant $[A] = a$
Order of reaction = 2
So rate of reaction = $k\,[A]^2 = ka^2$ ...(1)
(i) Given that concentration of the reactant is doubled
So, $[A] = 2a$,
Putting the value in equation (i) we get
New rate of reaction, $R_1 = k(2a)^2 = 4ka^2$
Hence, rate of reaction will increase to 4 times.
(ii) Given that concentration of the reactant is reduced to half
So, $[A] = (1/2)a$
Putting the value in equation (1), we get
New rate of reaction $R_2 = k((1/2)a)^2 = (1/4)ka^2$
Hence, rate of reaction will reduce to 1/4.

21. Let the rate law expression is $r = k[X]^a[Y]^b$
Given, $r_1 = k(0.1)^a\,(0.2)^b = 0.05$ ...(i)
$r_2 = k(0.2)^a\,(0.2)^a = 0.10$ ...(ii)
$r_3 = k(0.1)^a\,(0.1)^b = 0.05$ ...(iii)

From eqn. (i) and (ii), $\frac{r_2}{r_1} = \frac{0.10}{0.05} = 2^a \Rightarrow a = 1$

From eqn. (ii) and (iii), $\frac{r_1}{r_3} = \frac{0.05}{0.05} = 2^b \Rightarrow b = 0$

(i) Order w.r.t. X is one and w.r.t. Y is zero.
(ii) The rate law expression is $r = k[X]^1[Y]^0 = k[X]$

(iii) From the rate law, $k = \frac{\text{Rate}}{[X]} = \frac{0.05}{0.1} = 5 \times 10^{-3}\ \text{min}^{-1}$

22. (a) For a reaction involving a solid reactant or catalyst, the smaller is the particle size *i.e.*, greater is the surface area, the faster is the reaction. Therefore, on reducing the surface area, rate of reaction is reduced.

(b) A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. For a reversible reaction catalyst increases the speed of reaction in both forward and reverse reaction, which helps in attaining the equilibrium faster.

(c) The rate of reaction increases with increase in temperature. In most of the cases, the rate of reaction becomes nearly double for every 10°C rise of temperature. In some cases, reactions do not take place at room temperature but takes place at higher temperature.

23. (a) Let rate = $k[A]^x[B]^y$

$4.2 \times 10^{-2} = k(0.2)^x(0.3)^y$ ...(i)

$6.0 \times 10^{-3} = k(0.1)^x(0.1)^y$ ...(ii)

$1.68 \times 10^{-1} = k(0.4)^x(0.3)^y$ ...(iii)

$2.40 \times 10^{-2} = k(0.1)^x(0.4)^y$ ...(iv)

Dividing eqn. (iii) by (i),

$$\frac{1.68\times10^{-1}}{4.2\times10^{-2}} = \frac{(0.4)^x}{(0.2)^x}$$

or $4 = 2^x \Rightarrow x = 2$

Dividing eqn. (iv) by (ii),

$$\frac{2.40\times10^{y}}{6.0\times10^{y}} = \frac{(0.4)^y}{(0.1)^y} \text{ or } 4 = 4^y \Rightarrow y = 1$$

Hence, order of the reaction w.r.t. *A* is 2 and w.r.t. *B* is 1.

(b) Rate = $k[A]^2[B]^1$

Overall order of reaction = 2 + 1 = 3

(c) From experiment 1,

$4.2 \times 10^{-2} = k(0.2)^2(0.3)$

or $4.2 \times 10^{-2} = k \times 0.012$

or $k = 3.5$

24. Since the reaction is second order w.r.t. *A* and first order w.r.t. *B*.

(i) Differential rate equation is

Rate = $k[A]^2[B]$

(ii) The new concentration of *A* = [3*A*]

∴ New rate = $k[3A]^2[B] = 9k[A]^2[B]$

∴ New rate = 9 times of the original rate

(iii) New concentration of *A* = [2*A*]

New concentration of *B* = [2*B*]

∴ New rate = $k[2A]^2[2B] = 8k[A]^2[B]$

∴ New rate = 8 times of the original rate.

25. (c): Photochemical combination of hydrogen and chlorine to give hydrogen chloride is called zero order reaction because rate of reaction is independent of concentration of the reactants.

$$H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$$

26. (d): For zero order reaction rate constant is given by :

$$k = \frac{[R]_0 - [R]}{t}, \quad \text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$k = \frac{[R]_0 - \frac{[R]_0}{2}}{t_{1/2}} \Rightarrow k = \frac{[R]_0}{2t_{1/2}} \Rightarrow t_{1/2} = \frac{[R]_0}{2k}$$

In zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

27. (a): Hydrolysis of an ester is a pseudo first order reaction.

28. Half-life of first order reaction is independent of the initial concentration of reactants.

$$t_{1/2} = \frac{0.693}{k}$$

29. Slope = $-k$

Answer Tips

- The straight line graph is represented by the equation $y = mx + c$, where m represents the slope of the graph.

30. For first order reaction

$$k = \frac{2.303}{t}\log\frac{[R_0]}{[R]}$$

$$\log\frac{[R_0]}{[R]} = \frac{kt}{2.303}$$

Plotting $\log [R_0]/[R]$ *vs* t will give a straight line with slope $\frac{k}{2.303}$.

31. Those reactions which are not truly of the first order but under certain conditions become reactions of the first order are called *pseudo first order reactions.*

e.g., inversion of cane sugar :

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate = $k[C_{12}H_{22}O_{11}]^1[H_2O]^0$

32. (a) Unit of rate constant (k) = $(\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$

or $(\text{bar})^{1-n}\ \text{s}^{-1}$

For, $n = 2$, $k = \text{mol}^{-1}\ \text{L}\ \text{s}^{-1}$. Thus, this reaction is a second order reaction.

(b) For the reaction, $A \longrightarrow B$

Rate = $R = k[A]^2$ (As reaction is of second order.)

$R' = k[3A]^2 \Rightarrow R' = 9k[A]^2$

$$\frac{R'}{R} = 9$$

So, rate of reaction becomes 9 times by increasing concentration of *A* to three times.

(c) Integrated rate equation for zero order reaction is :

$[A]_t = -kt + [A]_0$

33. (a) The reaction is of first order.

(b) The rate of first order reactions and the concentration of the reactant vary exponentially with time. Hence, theoretically it will take infinite time for the reaction to go to completion (though after a finite period, the concentration becomes nearly zero).

34. Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.
Half-life of first order reaction is independent of the initial concentration of reactants.

$$t_{1/2} = \frac{0.693}{k}$$

35. The sum of the exponents (powers) to which the molar concentrations in the rate law equation are raised to express the observed rate of the reaction is called the order of reaction.
(a) For first order reaction, $t_{1/2} = k[R_0]^0 = k$
Thus, $t_{1/2}$ is independent of initial concentration. Hence, plot of $t_{1/2}$ *vs.* $[R_0]$ will be a horizontal line.
(b) For zero order reaction, $t_{1/2} = k[R_0]$
Hence, plot of $t_{1/2}$ *vs*, $[R_0]$ will be linear passing through the origin and having slope = *k*.

Key Points

- $t_{1/2} \propto \frac{1}{[R_0]^{(n-1)}}$
  where, *n* = order of reaction

36. (a) Given, rate = $5.5 \times 10^{-14}\,[C_2H_4]$
This implies that it is a first order reaction as rate depends on $[C_2H_4]$ only.
Hence, unit of rate constant is s^{-1} or $time^{-1}$.

(b) For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

or $t_{1/2} = \frac{0.693}{5.5\times10^{-14}} = 1.26 \times 10^{13}$ sec

37. (i) The reaction is of zero order.
(ii) Slope of the curve = $-k$

Concept Applied

- For zero order reaction,
  $[R]_t = -kt + [R]_0$

38. For first order reaction, $t = \frac{2.303}{k}\log\frac{[R_0]}{[R_t]}$
For 99% completion of reaction
$t = t_{0.99}$, $[R]_0 = 1$, $[R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

$$t_{0.99} = \frac{2.303}{k}\log\frac{1}{10^{-2}} = \frac{2.303}{k}\log 10^2 = \frac{2.303}{k}\times 2 \quad ...(i)$$

For 90% completion of reaction
$t = t_{0.90}$, $[R]_0 = 1$, $[R]_t = (1-0.9) = 0.1 = 10^{-1}$

$$t_{0.90} = \frac{2.303}{k}\log\frac{1}{10^{-1}} = \frac{2.303}{k}\log 10 = \frac{2.303}{k} \quad ...(ii)$$

Comparing equations (i) and (ii), $t_{0.99} = 2 \times t_{0.90}$

39. The time taken for half of the reaction to complete, *i.e.*, the time in which the concentration of a reactant is reduced to half of its original value is called half life period of the reaction.

(i) For zero order reaction rate constant is given by :

$$k = \frac{[R]_0 - [R]}{t}, \text{ At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$k = \frac{[R]_0 - \frac{[R]_0}{2}}{t_{1/2}} \Rightarrow k = \frac{[R]_0}{2t_{1/2}} \Rightarrow t_{1/2} = \frac{[R]_0}{2k}$$

For zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

(ii) For first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}, \text{ At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore \quad k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2} \text{ or, } t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303\times 0.3010}{k} \Rightarrow t_{1/2} = \frac{0.693}{k}$$

For first order reaction, $t_{1/2}$ is independent of initial concentration.

40. (a) Given : $\frac{-d[N_2O_5]}{dt} = 1.4 \times 10^{-3}\ Ms^{-1}$
According to rate law expression,

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\text{Rate of reaction} = \frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\times 1.4\times 10^{-3} Ms^{-1}$$
$$= 7 \times 10^{-4}\ Ms^{-1}$$

(b) For first order reaction, $t = \frac{2.303}{k}\log\frac{[R_0]}{[R_t]}$
For 99% completion of reaction
$t = t_{0.99}$, $[R]_0 = 1$, $[R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

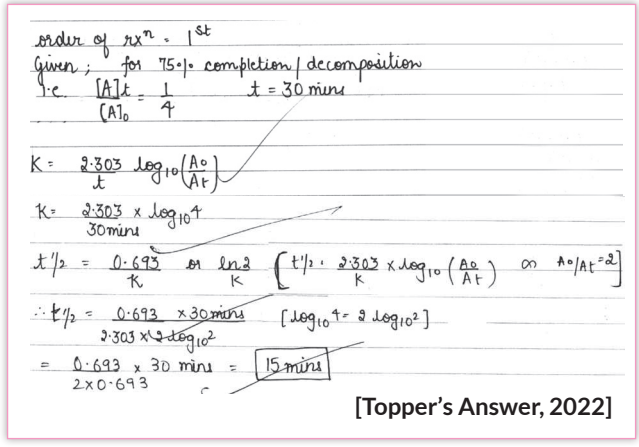
$$t_{0.99} = \frac{2.303}{k}\log\frac{1}{10^{-2}} = \frac{2.303}{k}\log 10^2 = \frac{2.303}{k}\times 2 \quad ...(i)$$

For 90% completion of reaction
$t = t_{0.90}$, $[R]_0 = 1$, $[R]_t = (1-0.9) = 0.1 = 10^{-1}$

$$t_{0.90} = \frac{2.303}{k}\log\frac{1}{10^{-1}} = \frac{2.303}{k}\log 10 = \frac{2.303}{k} \quad ...(ii)$$

Comparing equations (i) and (ii), $t_{0.99} = 2 \times t_{0.90}$

41.


order of rxn. 1st
Given ; for 75% completion / decomposition
i.e. [A]t/[A]0 = 1/4 t = 30 mins
K = 2.303/t log10(A0/At)
K = 2.303/30mins x log10 4
t1/2 = 0.693/K or ln2/K [t1/2 = 2.303/K x log10(A0/At) on A0/At=2]
∴ t1/2 = 0.693/2.303 x 30mins x 2 log10 2 [log10 4 = 2 log10 2]
= 0.693/2x0.693 x 30 mins = 15 mins

[Topper's Answer, 2022]

42. (a) This graph represents first order reaction.

(b) Slope of the curve is $\frac{k}{2.303}$

(c) $t_{1/2} = \frac{0.693}{k}$

43. $t_{1/2}$ or $t_{50\%}$ = 40 min

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{40} = 0.0173 \text{ min}^{-1}$$

$$t_{90\%} = \frac{2.303}{k}\log\frac{100}{100-90} = \frac{2.303}{0.0173}\log 10 = 133 \text{ min}$$

44. (i) The reaction is of zero order.

(ii) Slope of the curve = $-k$

(iii) Unit of rate constant, k, for zero order reaction is mol L^{-1} s^{-1}.

45. $$t = \frac{2.303}{k}\log\frac{A_0}{A_t}$$

$$t = \frac{2.303}{4.9\times10^{-3}}\log\frac{4}{3}$$

t = 58.75 s

46. According to the 1st order kinetics,

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$$

or, $$k = \frac{2.303}{80}\log\frac{100}{60} = 6.386 \times 10^{-3} \text{ min}^{-1}$$

Time required for 90% completion of the reaction,

$$t = \frac{2.303}{k}\log\frac{100}{10} = \frac{2.303}{6.386\times10^{-3}}\log 10 = 360.63 \text{ minutes.}$$

47. For a zero order reaction, $k = \frac{1}{t}([A]_0 - [A])$

$$\Rightarrow \quad t = \frac{1}{4\times10^{-3}}\times(0.1-0.064) = 9 \text{ s}$$

48. For a first order reaction, $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

$$k = \frac{2.303}{30}\log\frac{100}{100-20} = \frac{2.303}{30}\times0.097 = 7.4 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7.4\times10^{-3}} = 93.65 \text{ min}$$

Commonly Made Mistake

- The units of time and rate should be kept uniform.

49. (a) The formula of rate constant for first order reaction is

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$$

$$k_1 = \frac{2.303}{300 \text{ s}}\log\frac{(1.6\times10^{-2}) \text{ mol L}^{-1}}{(0.8\times10^{-2}) \text{ mol L}^{-1}} = 2.3\times10^{-3} \text{ s}^{-1}$$

Similarly, $$k_2 = \frac{2.303}{600 \text{ s}}\log\frac{(1.6\times10^{-2}) \text{ mol L}^{-1}}{(0.4\times10^{-2}) \text{ mol L}^{-1}}$$

$$= 2.3 \times 10^{-3} \text{ s}^{-1}$$

Unit and magnitude of rate constant shows the given reaction is of first order.

(b) The formula for half-life for first order reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.3\times10^{-3} \text{ s}^{-1}} = 301.30 \text{ s}$$

50. According to the 1st order kinetics

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A_t]}$$

$$\Rightarrow \quad k = \frac{2.303}{20 \text{ min}}\log\frac{[100]}{[75]} \Rightarrow k = 0.014 \text{ min}^{-1}$$

Similarly, for 2nd process, $0.014 = \frac{2.303}{t}\log\left(\frac{100}{25}\right)$

t = 99 min

Commonly Made Mistake

- A_t = conc. at time t, *i.e.*, $[A]_0 - [X]$
  Where $[X]$ = conc. of reactant that has been decomposed.

51. The given reaction is

$$C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$$

At time t = 0	0.30	0	0
At time t = 300 sec	0.30 – x	x	x

Total pressure = 0.30 – x + x + x = 0.50 atm

or 0.30 + x = 0.50

$\therefore$ x = 0.50 – 0.30 = 0.20

$\therefore$ Initial pressure, P_0 = 0.30 atm

Pressure of C_2H_5Cl after 300 sec,

P_t = 0.30 – 0.20 = 0.10 atm

Using formula for first order reaction,

$$k = \frac{2.303}{t}\log\frac{P_0}{P_t}$$

$$k = \frac{2.303}{300}\log\frac{0.30}{0.10}$$

$$k = \frac{2.303}{300}\log 3 = \frac{2.303\times0.4771}{300} = 3.66 \times 10^{-3} \text{ sec}^{-1}$$

Concept Applied

- For a typical first order gas phase reaction, the concentration term can be replaced by pressure term.

52. $t_{50\%}$ or $t_{1/2}$ = 30 minutes

$$\Rightarrow \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

$$t_{90\%} = \frac{2.303}{k}\log\frac{100}{100-90} = \frac{2.303}{0.0231}\log 10$$

= 99.69 minutes

53. For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = \frac{2.303}{10}\log\frac{100}{100-25}$$

$$k = \frac{2.303}{10}\times0.124 = 0.003$$

$\therefore$ $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.003} = 23.1 \text{ min}$$

54. (i) The reaction is of 1st order.

(ii) For first order reaction

$\ln[R] = -kt + \ln [R]_0$

comparing eqn. $y = mx + c$

we get a straight line with slope = $-k$ and intercept equal to $\ln[R]_0$.

(iii) Unit of rate constant for first order reaction

$$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$$

55. $$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow \quad k = 60\ \text{s}^{-1}, [R] = \frac{1}{10}[R]_0$$

$$t = \frac{2.303}{60} \log \frac{[R]_0}{\frac{[R]_0}{10}} \quad \Rightarrow \quad t = \frac{2.303}{60} \log 10$$

$$\Rightarrow \quad t = \frac{2.303 \times 1}{60} = 0.0384 \text{ second}$$

56. The given reaction is

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

At $t = 0$	0.4 atm	0	0
At time t	(0.4 – x) atm	x atm	x atm

Total pressure at time t will be

$P_t = (0.4 - x) + x + x = 0.4 + x$

$x = (P_t - 0.4)$

Pressure of SO_2Cl_2 at time t will be

$p_{SO_2Cl_2} = 0.4 - x = 0.4 - (P_t - 0.4) = 0.8 - P_t$

At time t = 100 s, P_t = 0.7 atm

$\therefore \quad p_{SO_2Cl_2} = 0.8 - 0.7 = 0.1$ atm

According to first order kinetic equation

$$k = \frac{2.303}{t} \log \frac{p_{SO_2Cl_2(\text{initial})}}{p_{SO_2Cl_2(\text{after reaction})}}$$

$$= \frac{2.303}{100} \log \left(\frac{0.4}{0.1}\right) = 1.3 \times 10^{-2}\ \text{s}^{-1}$$

57. (i) $$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Given $k = 1.06 \times 10^{-3}\ \text{min}^{-1}$, $\frac{[A]_0}{[A]} = \frac{100}{85}$

$$t = \frac{2.303}{1.06 \times 10^{-3}\ \text{min}^{-1}} \log \frac{100}{85}$$

$$t = \frac{2303}{1.06}[2 \log 10 - \log 85]\ \text{min}$$

$$t = \frac{2303}{1.06}[2 \times 1 - 1.9294] = \frac{2303 \times 0.0706}{1.06}$$

t = 153.39 min = 153.4 min

(ii) Given $k = 1.06 \times 10^{-3}\ \text{min}^{-1}$, $\frac{[A]_0}{[A]} = \frac{100}{15}$

$$t = \frac{2.303}{1.06 \times 10^{-3}\ \text{min}^{-1}} \log \frac{100}{15}$$

$$= \frac{2303}{1.06}[2 \log 10 - \log 15]\ \text{min}$$

$$= \frac{2303}{1.06}[2 \times 1 - 1.1761] = \frac{2303 \times 0.8239}{1.06}\ \text{min} = 1790\ \text{min}$$

58. (i) Average rate of reaction : Ratio of change in concentration and time required for the change is average rate of reaction.

$$r_{av} = \frac{\Delta x}{\Delta t} = \frac{\text{Change in concentration}}{\text{Time required for the change}}$$

(ii) Two factors that affect rate of reaction are:

(a) Nature of reactants

(b) Temperature

(iii) (1) The rate of reaction of a zero order reaction is proportional to zero power of the concentration of reactants. Rate of reaction for zero order reaction is given as :

$$k = \frac{[R]_0 - [R]}{t}$$

(2) Units of k for zero order reaction is mol $L^{-1}s^{-1}$.

OR

(iii) (1) $P + 2Q \longrightarrow$ Products

Rate = $k[P]^{1/2}[Q]^1$

Order of reaction = $\frac{1}{2} + 1 = 3$

(2) The reactions which are of second order but behave like first order reactions are called pseudo first order reactions *e.g.*, during hydrolysis of ethyl acetate (ester) with water, the concentration of water does not alter much during the reaction. So, in the rate equation, the rate of change in water concentration (the reactant which is in excess) can be taken as constant hence the reaction behaves as first order reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate = $k'[CH_3COOC_2H_5][H_2O]$ the term $[H_2O]$ can be taken as constant. Hence, the rate equation becomes

Rate = $k[CH_3COOC_2H_5]$ where $k = k'[H_2O]$.

59. (i) Rate = $k[A]^{\frac{1}{2}}[B]^{\frac{3}{2}}$

Because reaction is an elementary reaction, hence order of reaction will be $\frac{1}{2} + \frac{3}{2} = 2$

(ii) Rate of reaction increases with increase in temperature.

(iii) Rate of reaction is the rate of change in concentration of a reactant or product in unit time.

(iv) (a) For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} = 77.78\ \text{min}$$

$k = 8.90 \times 10^{-3}\ \text{min}^{-1}$

Time required for 30% completion,

$$t = \frac{2.303}{k} \log \left(\frac{100}{70}\right) = \frac{2.303}{8.90 \times 10^{-3}\ \text{min}^{-1}} \log 1.43$$

t = 40 min

OR

(b) Given :

For first order reaction, $k = 1 \times 10^{-3}\ sec^{-1}$

$$t = \frac{2.303}{k}\log\frac{[A_o]}{[A]}$$

$$t = \frac{2.303}{1\times10^{-3}\,sec^{-1}}\log\left(\frac{5}{3}\right) = \frac{2.303\times0.2219}{1\times10^{-3}\,sec^{-1}} = 511.03\ sec$$

60. (a) The rate of reaction is nearly doubled with a rise in temperature by 10°C for a chemical reaction. The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

$$k = Ae^{-E_a/RT}$$

where $k \rightarrow$ Rate constant

$A \rightarrow$ Arrhenius factor

$R \rightarrow$ Gas constant

$T \rightarrow$ Temperature

$E_a \rightarrow$ Energy of activation for the reaction.

(b) Rate = $k[A]^2[B]^{1/2}$

As order of reaction is sum of powers of concentration represented in rate law, order of the given reaction will be $2+\frac{1}{2} = \frac{5}{2} = 2.5$

(c) Differences between order and molecularity of a reaction are the following :

	Order of a reaction	Molecularity of a reaction
1.	It is the sum of powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2.	It can be zero or even a fraction.	It is always a whole number.

(d) Given that, reaction is of first order,

$k = 2 \times 10^{-3}\ sec^{-1}$

$[A]_0 = 6$ g, $[A]_t = 2$ g

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]_t} \Rightarrow t = \frac{2.303}{2\times10^{-3}}\times\log\left(\frac{6}{2}\right)$$

$t = 1.15 \times 10^3 \times (0.4771)$

$t = 0.5486 \times 10^3\ sec = 548.6\ s$

OR

Given that, $t_{1/2} = 6930$ years

$[A]_t = 0.75 \quad [A]_0 = 1$

$$t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{6930}$$

$k = 1 \times 10^{-4}\ year^{-1}$

$$t = \frac{2.303}{k}\log\frac{[A_0]}{[A]} = \frac{2.303}{10^{-4}}\times\log\left[\frac{1}{0.75}\right]$$

$$t = 2.303 \times 10^4 \times \log\left(\frac{100}{75}\right) = 2.303 \times 10^4 \times \log\left(\frac{4}{3}\right)$$

$t = 2.303 \times 10^4 \times (\log 4 - \log 3)$

$t = 2.303 \times 10^4 \times (0.6021 - 0.4771)$

$t = 0.2878 \times 10^4 \Rightarrow t = 2878$ years

61. (a) $t = 40$ minutes

$[A_0] = 100 \quad [A_t] = 75$

For first order reaction

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A_t]} = \frac{2.303}{40}\log\left(\frac{100}{75}\right)$$

$$= \frac{2.303}{40}\log\frac{4}{3} = \frac{2.303}{40}(\log 4 - \log 3)$$

$$= \frac{2.303}{40}(0.6020 - 0.4771)$$

$k = 7.19 \times 10^{-3}\ min^{-1}$

$$t = \frac{2.303}{k}\log\frac{[A_0]}{[A_t]}$$

For 80% completion $[A_0] = 100, \quad [A_t] = 20$

$$t = \frac{2.303}{7.19\times10^{-3}}\log\frac{100}{20} = \frac{2.303}{7.19\times10^{-3}}\times0.6990$$

$t = 223.8$ minute

(b) Order of reaction : The sum of exponents (powers) to which the molar concentration in the rate law equation are raised to express the observed rate of the reaction is called the order of reaction.

If one of the reactant is taken in large excess then its concentration will not affect the rate of reaction, thus the bimolecular reaction will follows first order kinetics.

Example,

$$\underset{}{C_{12}H_{22}O_{11}} + \underset{\text{Excess}}{H_2O} \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate = $k[C_{12}H_{22}O_{11}]$

62. (a) (i) The reaction is of 1^{st} order.

(ii) For first order reaction

$\ln[R] = -kt + \ln[R]_0$

comparing eqn. $y = mx + c$

we get a straight line with slope = $-k$ and intercept equal to $\ln[R]_0$.

(iii) Unit of rate constant for first order reaction

$$\frac{mol\,L^{-1}}{s}\times\frac{1}{(mol\,L^{-1})^1} = s^{-1}$$

(b) For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = \frac{2.303}{25}\log\frac{100}{100-25}$$

$$k = \frac{2.303}{25}\times0.125 = 0.0115$$

$$\therefore \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0115} = 60.26\,min$$

63. (i) For a first order reaction, $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$

When $t = 30$ s

$$k = \frac{2.303}{30}\log\frac{0.60}{0.30} = \frac{2.303}{30}\times0.3010 = 0.0231\ s^{-1}$$

When t = 60 s

$$k = \frac{2.303}{60}\log\left(\frac{0.60}{0.15}\right) = \frac{2.303}{60} \times 0.6021 = 0.0231\ s^{-1}$$

As the value of k is constant at different time intervals, the reaction is first order *w.r.t.* ester when $[H_2O]$ is constant. Hence, it is pseudo first order reaction.

(ii) Average rate $= -\frac{C_2 - C_1}{t_2 - t_1} = \frac{-(0.15 - 0.30)}{60 - 30}$

$$= \frac{0.15}{30} = 5 \times 10^{-3}\ mol\ L^{-1}s^{-1}$$

64. (c): In the presence of a catalyst, the reaction follows a path of lower activation energy.

65. (d): Data is insufficient,
E_a can't be predicted.

66. No

67. (a) A catalyst lowers the activation energy (E_a) by providing an alternate pathway or reaction mechanism.
(b) Catalyst does not affect the Gibbs energy (ΔG) of a reaction.

68. The minimum extra energy which must be supplied to the reactants to enable them to cross over the potential energy barrier between reactants and products is called activation energy. It is denoted by E_a.

$E_a = E_T - E_R$

69. The rate constant of a chemical reaction is nearly doubled with a rise in temperature by 10°.
The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

$k = Ae^{-E_a/RT}$

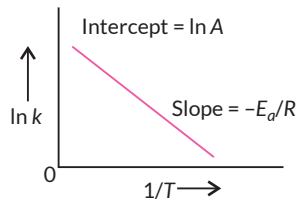
where $k \rightarrow$ Rate constant
$A \rightarrow$ Arrhenius factor
$R \rightarrow$ Gas constant
$T \rightarrow$ Temperature
$E_a \rightarrow$ Energy of activation for the reaction.

With increase in temperature, activation energy decreases.
Activation energy = Threshold energy — Average energy possessed by molecules.

70. $\ln k = -\frac{E_a}{RT} + \ln A$

Intercept = ln A

Slope = $-\frac{E_a}{R}$



Key Points

- Arrhenius equation : $k = Ae^{-E_a/RT}$

71. The rate of reaction is nearly doubled with a rise in temperature by 10°C for a chemical reaction.
The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

$k = Ae^{-E_a/RT}$

where $k \rightarrow$ Rate constant
$A \rightarrow$ Arrhenius factor
$R \rightarrow$ Gas constant
$T \rightarrow$ Temperature
$E_a \rightarrow$ Energy of activation for the reaction.

72. $k = (2.5 \times 10^{14})\, e^{\frac{-25000}{T}}$

Comparing it with the Arrhenius equation

$k = Ae^{-E_a/RT}$

We get $A = 2.5 \times 10^{14}\ s^{-1}$

$$\frac{E_a}{R} = 25000$$

or $E_a = 25000\ K \times 8.314\ J\ K^{-1}\ mol^{-1} = 207850\ J\ mol^{-1}$

For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

or, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{300} = 2.31 \times 10^{-3}\ min^{-1}$

Concept Applied

- In order to calculate E_a in J/mol, the value of R should be taken as 8.314 J/mol K.

73. Since the rate of a reaction quadruples when temperature changes from 293 K to 313 K,

$\therefore \quad k_2 = 4k_1$

$T_1 = 293$ K and $T_2 = 313$ K

According to Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Putting the values,

$$\log\frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314\ JK^{-1}\ mol^{-1}}\left[\frac{(313-293)K}{293K \times 313K}\right]$$

$$0.6021 = \frac{E_a \times 20\,K}{2.303 \times 8.314\ J\ K^{-1}\ mol^{-1} \times 293\,K \times 313\,K}$$

$$\therefore \quad E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}\ J\,mol^{-1}$$

$= 52863.3\ J\ mol^{-1} = 52.86\ kJ\ mol^{-1}$

74. Given, $T_1 = 300$ K, $T_2 = 320$ K
$k_1 = 2 \times 10^{-2}$, $k_2 = 6 \times 10^{-2}$, $E_a = ?$

Using Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or $$\log\frac{6 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{320}\right]$$

or $$\log 3 = \frac{E_a}{2.303 \times 8.314} \times \left[\frac{320 - 300}{320 \times 300}\right]$$

or $$E_a = \frac{0.4771 \times 2.303 \times 8.314 \times 320 \times 300}{20}$$

$= 43848\ J\ mol^{-1} = 43.85\ kJ\ mol^{-1}$

75. $(t_{1/2})_1 = 40$ min, $(t_{1/2})_2 = 20$ min
$T_1 = 300$ K, $T_2 = 320$ K

E_a = ?

For 1st order reaction,

$$k_1 = \frac{0.693}{(t_{1/2})_1} = \frac{0.693}{40} = 0.017\ \text{min}^{-1}$$

$$k_2 = \frac{0.693}{(t_{1/2})_2} = \frac{0.693}{20} = 0.034\ \text{min}^{-1}$$

From Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{0.034}{0.017} = \frac{E_a}{2.303\times 8.314}\left[\frac{20}{320\times 300}\right]$$

$$E_a = \frac{0.3010\times 2.303\times 8.314\times 320\times 300}{20}$$

E_a = 27663.8 J/mol = 27.6 kJ/mol

76. For first order reaction, $t_{1/2} = \frac{0.693}{k}$

$t_{1/2} = 200\ \text{min} = 200\times 60 = 12000\ \text{s}$

$$\Rightarrow \quad k = \frac{0.693}{12000\ \text{s}} = 5.8\times 10^{-5}\ \text{s}^{-1}$$

Also, for first order decomposition of H_2O_2, rate constant is

$$\log k = 14.2 - \frac{1.0\times 10^4}{T}\text{K}$$

Comparing the above equation with the Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

or $$\frac{E_a}{2.303\,RT} = \frac{1\times 10^4}{T}$$

$$\Rightarrow \quad E_a = 2.303\times 8.314\times 1.0\times 10^4 = 1.91\times 10^5\ \text{J mol}^{-1}$$

77. Given, T_1 = 300 K, T_2 = 310 K

$k_1 = 2\times 10^{-2}$, $k_2 = 4\times 10^{-2}$, E_a = ?

Using Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or $$\log\frac{4\times 10^{-2}}{2\times 10^{-2}} = \frac{E_a}{2.303\times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

or $$\log 3 = \frac{E_a}{2.303\times 8.314}\times\left[\frac{320-300}{320\times 300}\right]$$

or $$E_a = \frac{0.301\times 2.303\times 8.314\times 310\times 300}{10}$$

$$= 53598\ \text{J mol}^{-1} = 53.6\ \text{kJ mol}^{-1}$$

78. $k_1 = 0.02\ \text{s}^{-1}$, $k_2 = 0.07\ \text{s}^{-1}$

T_1 = 500 K, T_2 = 700 K

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

$$\log\frac{0.07}{0.02} = \frac{E_a}{2.303R}\left[\frac{700-500}{700\times 500}\right]$$

$$E_a = \frac{0.544\times 2.303\times 8.314\times 700\times 500}{200}$$

$$= 18228.07\ \text{J mol}^{-1} = 18.23\ \text{kJ mol}^{-1}$$

79. $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$E_a = \left(\frac{2.303\times R\times T_1\times T_2}{T_2 - T_1}\right)\log\frac{k_2}{k_1}$$

$$E_a = \frac{2.303\times 8.314\times 650\times 700}{700-650}\times\log\frac{2.39\times 10^{-8}}{2.15\times 10^{-8}}$$

$$E_a = \frac{19.147\times 650\times 700}{50}(\log 2.39 - \log 2.15)\ \text{J mol}^{-1}$$

$$= 174237.7\ (0.3783 - 0.3324)\ \text{J mol}^{-1}$$

$$= 174237.7\times 0.0459\ \text{J mol}^{-1} = 7997.51\ \text{J mol}^{-1}$$

80. (a) $$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$$

$$\Rightarrow \quad k = 60\ \text{s}^{-1}, [R] = \frac{1}{16}[R]_0$$

$$t = \frac{2.303}{60}\log\frac{[R]_0}{\frac{[R]_0}{16}} \quad \Rightarrow \quad t = \frac{2.303}{60}\log 16$$

$$\Rightarrow \quad t = \frac{2.303\times 1.20}{60} = 0.046\ \text{second}$$

(b) Following factors affect the rate of a chemical reaction :

(i) Concentration of reactants : Higher the concentration of reactants, faster would be the rate of reaction.

Rate = $k\,C^n$, where C = concentration of reactant.

(ii) Temperature : The rate of reaction increases with the temperature. For every 10°C rise in temperature rate of reaction increases 2 to 3 times.

(c) Two conditions for the collisions to be effective collisions are:

(i) Colliding molecules must have energy greater than the threshold energy.

(ii) Colliding molecules must have proper orientations at the time of collision.

CBSE Sample Questions

1. **(a):** Rate = $[A]^2[B]^0 \Rightarrow$ Rate = $[A]^2$

If $[A]$ is doubled then, Rate = $[2A]^2$ become $4[A]^2$ = 4 Rate

Rate of reaction increases 4 times.

Note : Order of B is not mentioned in question. **(1)**

2. (a) The rate of reaction will increase. The catalyst decreases the activation energy of the reaction therefore the reaction becomes faster. **(1)**

(b) The rate of reaction will decease. At lower temperatures, the kinetic energy of molecules decrease

thereby, the collisions decrease resulting in lowering of rate of reaction. **(1)**

3. (i) Rate = $k[A][B]^{1/2}$ **(1/2)**

$\therefore$ Order of reaction = 1 + 1/2 = 1.5

Molecularity of the reaction cannot be 1.5. **(1/2)**

Since the reaction occurs in steps hence, it is a complex reaction.

(ii) Units of k = $mol^{-1/2}\ L^{1/2}\ s^{-1}$ **(1)**

4. Given reaction, $P + 2Q \rightarrow R + 2S$

Exp.	Initial P (mol/L)	Initial Q (mol/L)	Initial Rate of Formation of R (M min^{-1})
1.	0.10	0.10	3.0×10^{-4}
2.	0.30	0.30	9.0×10^{-4}
3.	0.10	0.30	3.0×10^{-4}
4.	0.20	0.40	6.0×10^{-4}

Let rate of this reaction, $r = k[P]^x\ [Q]^y$

Then, $\frac{r_1}{r_3} = \frac{3.0\times10^{-4}}{3.0\times10^{-4}} = \frac{k(0.10)^x(0.10)^y}{k(0.10)^x(0.30)^y}$

$\Rightarrow \quad 1 = \left(\frac{1}{3}\right)^y \quad \Rightarrow \quad y = 0$ **(1/2)**

Again from $\frac{r_2}{r_3} = \frac{9.0\times10^{-4}}{3.0\times10^{-4}} = \frac{k(0.30)^x(0.30)^y}{k(0.10)^x(0.30)^y}$ **(1/2)**

$\Rightarrow \quad 3.0 = (3)^x \Rightarrow x = 1$

Hence, the expression for rate law is, $r = k[P]$ **(1)**

5. (a): The rate constant for the decay of O-15 is less than that for O-19. Therefore, the rate of decay of O-15 will be slower and will have a longer half life. **(1)**

6. Half life, $t_{1/2} = 0.693/k$

$k = 0.693/69.3 = 1/100 = 0.01\ min^{-1}$ **(1/2)**

For first order reaction,

$k = \frac{2.303}{t}\log\frac{[R_o]}{R}$ **(1/2)**

$t = \frac{2.303}{0.01}\log\frac{100}{20}$

$t = 230.3 \log 5 \qquad (\log 5 = 0.6990)$ **(1/2)**

$t = 160.9$ min **(1/2)**

7. For first order reaction, $k = 0.693/t_{1/2}$

$k = 0.693/5730\ years^{-1}$ **(1/2)**

$t = \frac{2.303}{k}\log\frac{C_0}{C_t}$ **(1/2)**

Let $C_0 = 1$, $C_t = 3/10$,

so, $\frac{C_0}{C_t} = \frac{1}{3/10} = \frac{10}{3} \Rightarrow t = \frac{2.303}{0.693}\times5730\log\frac{10}{3}$ **(1/2)**

$t = 19042\ (1 - 0.4771) = 9957$ years **(1/2)**

8. (a) Ratio of neutrons to protons in carbon-14 is 2.3: 1 which makes it unstable whereas in carbon-12 this ratio is 1 : 1, *i.e.*, number of neutrons and protons are equal. Hence C-12 nucleus is stable. **(1)**

(b) The age of fossils can be estimated with the help of C-14 decay. All living organisms have C-14 which continously decays. Once the organism dies, the decayed C-14 cannot be replaced back. **(1)**

(c) Carbon-14 atoms decay to stable nitrogen atoms and potassium-40 atoms decay to stable calcium atoms.

$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$ (β decay) **(1)**

$^{40}_{19}K \longrightarrow {}^{40}_{20}Ca + {}^{0}_{-1}e$ (β decay)

(d) $C_0 = 20$ g and C_t = ?

$t = 10320$ years, $k = \frac{0.693}{t_{1/2}} = 0.693/6000$

(half-life given in passage)

$t = \frac{2.303}{k}\log\frac{C_0}{C_t}$ **(1/2)**

$10320 = \frac{2.303}{\frac{0.693}{6000}}\log\frac{20}{C_t}$ **(1/2)**

$0.517 = \log\frac{20}{C_t} \Rightarrow \text{antilog } 0.517 = \log\frac{20}{C_t}$ **(1/2)**

$3.289 = \frac{20}{C_t} \Rightarrow C_t = 6.089$ g **(1/2)**

OR

$C_0 = 32$ g and $C_t = 12$ g

t = ? $k = 0.693/6000$ (half life given in passage)

$t = (2.303/k)\log(C_0/C_t)$ **(1/2)**

$t = 2.303 / (0.693/6000)\log(32/12)$ **(1/2)**

$t = \frac{2.303\times6000}{0.693}\log 2.667$ **(1/2)**

$t = \frac{2.303\times6000\times0.4260}{0.693} = 8494.64$ years **(1/2)**

9. (c) : $k = Ae^{-E_a/RT}$

$\ln k = \ln A - \frac{E_a}{RT}$

Comparing with $y = mx + c$

$m = -\frac{E_a}{RT}$ = Slope

Intercept = $c = \ln A$ **(1)**

Self Assessment

Case Based Questions (5 marks)

1. Read the passage given below and answer the following questions :

According to the collision theory for a chemical reaction to occur there must be collisions among the reactant molecules. However most of the collisions taking place among the reactant molecules are ineffective, only those collisions result in chemical reactions in which the colliding molecules are associated with a certain minimum energy called the threshold energy. When molecules having this energy collide, there is loosening or breaking of bonds resulting in a chemical reaction.

However there are some molecules which have much less kinetic energy than the threshold energy. Activation energy is given as :

Activation energy = Threshold energy

– Energy actually possessed by molecules

For exothermic reactions the energy of product is less than that of the reactant whereas for endothermic reactions energy of products is higher than that of the energy of reactants.

(i) The difference of energy between _____ and that of _____ is called energy of activation for forward reaction.

(a) Activated complex, normal energy of reactant
(b) Activated complex, normal energy of product
(c) Reactant and product
(d) Normal energy of product and threshold energy.

(ii) The activation energy of a reaction may be lowered by

(a) decreasing the temperature
(b) increasing the temperature
(c) adding a catalyst
(d) reducing the potential energy.

(iii) According to the collision theory of chemical reactions

(a) a chemical reaction occurs with every molecular collision
(b) rate is directly proportional to the number of collisions per second
(c) reactions in the gas phase are always of zero order
(d) none of these.

(iv) The activation energy for a simple chemical reaction

$A \longrightarrow B$ is E_a in forward direction. The activation energy for the backward reaction

(a) is always less than E_a
(b) can be less than or more than E_a
(c) is always double of E_a
(d) is negative of E_a.

(v) It has been found that for a chemical reaction with rise in temperature by 10°C, the rate constant is

(a) nearly doubled (b) nearly tripled
(c) increases 5 times (d) increases 4 times.

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

2. Assertion : For the first order reaction, half-life period is expressed as $(t)_{1/2} = \frac{2.303}{k}\log 2$.

Reason : The half-life time of a first order reaction is not always constant and it depends upon the initial concentration of reactants.

3. Assertion : The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ is 2.

Reason : The order of this reaction is 3/2.

Multiple Choice Questions (1 mark)

4. The half-life of a reaction is halved as the initial concentration of the reactant is doubled. The order of reaction is

(a) 0.5 (b) 1 (c) 2 (d) 0

5. If initial concentration is reduced to $1/4^{th}$ in a zero-order reaction, the time taken for half the reaction to complete

(a) remains same (b) becomes 4 times
(c) becomes one-fourth (d) doubles.

OR

The rate constant of a first order reaction is given by

(a) $k = 2.303 \times t \times \log_{10} \frac{a}{(a-x)}$

(b) $\frac{k}{t} = 2.303\log_{10}\frac{a}{(a-x)}$

(c) $k = \frac{2.303}{t}\log_{10}\frac{1}{(a-x)}$

(d) $k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$

6. For a reaction of order n, the unit of the rate constant is
(a) $mol^{1-n}L^{n-1}s^{-1}$ (b) $mol^{1-n}L^{1-n}s^{-1}$
(c) $mol^{1-n}L^{1-n}s$ (d) $mol^{1-n}L^{2n}s^{-1}$

7. For the reaction $A + B \longrightarrow C$, the following data for rate was obtained:

[A] (mol L^{-1})	[B] (mol L^{-1})	Rate (mole/litre sec)
2.0	3.0	0.10
6.0	3.0	0.90
6.0	6.0	0.90

the rate expression from the data is
(a) rate = $k[A][B]^2$ (b) rate = $k[A]^2$
(c) rate = $k[A][B]$ (d) rate = $k[B]^2[A]^0$

VSA Type Questions (1 mark)

8. Why the reaction is slow in some cases regardless of having a large number of colliding molecules with threshold energy?
9. What do you mean by rate determining step?
10. In what condition order and molecularity of a reaction become equal?
11. Define rate law.

SA I Type Questions (2 marks)

12. In the reaction : $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$, if the rate of formation of NO is 3.6×10^{-3} mol $L^{-1}s^{-1}$, calculate the
(a) rate of disappearance of NH_3 and
(b) rate of formation of H_2O.
13. Show that half life period of a first order reaction is independent of initial concentration of the reactant.
14. What is activation energy? How is it calculated?
15. For a homogeneous gas phase reaction
$A_{(g)} \rightarrow B_{(g)} + C_{(g)} + D_{(g)}$, the pressure of the reaction mixture increases by 40% in 20 minutes. Calculate rate constant of a reaction.
16. Rate of a reaction $A + B \rightarrow$ Products, increases two fold when concentration of A is doubled and by four fold when concentration of B is doubled. Predict the order of reaction.

OR

Write the expression for relation between $\log_{10}[R]$ and t for a first order reaction and draw a graph.

SA II Type Questions (3 marks)

17. (a) What is average rate of reaction?
(b) Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?
18. (i) (a) What is the drawback of collision theory?
(b) Mention the necessary conditions for collision of reactant molecules to give product.
(ii) What is catalyst? What is the effect of catalyst on the rate of a reaction?
19. Half life period of first order reaction at 47°C is 10 min and at 27°C is 30 min. Calculate the activation energy of the reaction.
20. A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.

OR

A certain reaction takes 5 minutes for initial concentration 0.5 mol L^{-1} to become 0.25 mol L^{-1} and another 5 minutes to becomes 0.125 mol L^{-1}. What is the order and specific rate constant of the reaction?

Case Based Questions (4 marks)

21. **Read the passage given below and answer the following questions :**
For the first order decomposition reaction,
$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2CH_3COCH_3 + C_2H_6$
In the gaseous phase, the pressures of the system at $t = 0$ and $t = 15$ min were found to be 169.3 Torr and 256 Torr, respectively.
(a) Give expression for the pressure of C_2H_6.
(b) Write integrated rate law expression for this reaction.
(c) Calculate rate constant k.

OR

Calculate the pressure of C_2H_6 at time t.

LA Type Questions (5 marks)

22. (i) State the role of activated complex in a reaction and state its relation with activation energy.
(ii) At room temperature (20°C) milk turns sour in about 64 hours. In a refrigerator at 3°C milk can be stored three times as long before it sours. Estimate the activation energy of the reaction that causes the souring of milk.
23. (i) The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for

the initial concentration of *A* to fall from 0.10 M to 0.075 M?

(ii) The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate (a) the specific rate constant, (b) the time at which 10 percent of the original material remains unreacted, (c) the time it takes for the next 20 percent, of the reactant left after the first 15 minutes, to react.

24. (i) What is the effect of temperature on the reaction rate?

(ii) In the Arrhenius equation for a certain reaction, the values of *A* and E_a (activation energy) are $4 \times 10^{13}\ s^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be ten minutes?

25. (i) What is zero order reaction? Give one example of zero order reaction.

(ii) The rate of decomposition of ammonia is found to depend upon the concentration of NH_3 according to the equation

$$-\frac{d[NH_3]}{dt} = \frac{k_1[NH_3]}{1+k_2[NH_3]}$$

What will be the order of reaction when

(a) concentration of NH_3 is very high?

(b) concentration of NH_3 is very low?

OR

(i) With the help of an example explain what is meant by pseudo first order reaction.

(ii) Write expression for rate constant of a zero order reaction and explain the terms involved. What is the unit of rate constant of a zero order reaction?

Detailed SOLUTIONS

1. (i) (a)

(ii) (c): In the presence of a catalyst, the reaction follows a path of lower activation energy.

(iii) (b)

(iv) (b): Can be less than or more than E_a depending whether the reaction is exothermic or endothermic.

(v) (a)

2. (c): For a first order reaction

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$k = \frac{2.303}{(t)_{1/2}}\log\frac{a}{a-a/2} = \frac{2.303}{(t)_{1/2}}\log\frac{a}{a/2} = \frac{2.303}{(t)_{1/2}}\ \log 2$$

Therefore half-life period $(t)_{1/2} = \frac{2.303}{k}\log 2.$

Thus, $(t)_{1/2}$ is independent of initial concentration of reactant for first order reaction.

3. (b): Generally, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation or it can also be defined as "the minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products." In case of $H_2 + Br_2 \rightarrow 2HBr$, molecularity is two. Order does not depend upon molecularity or vice-versa, it is an experimentally determined quantity.

4. (c): For n^{th} order reaction

$$t_{1/2} \propto \frac{1}{a^{n-1}};\ \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[a_2]^{n-1}}{[a_1]^{n-1}} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

$$\frac{t_{1/2}}{1/2t_{1/2}} = \left(\frac{2a}{a}\right)^{n-1} \Rightarrow 2 = (2)^{n-1} \Rightarrow (n-1) = 1 \Rightarrow n = 2$$

5. (c): For zero order reactions, $t_{1/2} = \frac{a}{2k}$

i.e. $t_{1/2} \propto a$

Therefore, when *A* is reduced to $\frac{1}{4}$th, $t_{1/2}$ will become $\frac{1}{4}$th.

OR

(d)

6. (a): For n^{th} order reaction,

Rate = $k[a]^n$

$$k = \frac{\text{Rate}}{[a]^n} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^n} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol}^n\text{L}^{-n}} = \text{mol}^{1-n}\,\text{L}^{n-1}\,\text{s}^{-1}$$

7. (b): Rate = $k\,[A]^m\,[B]^n$

$R_1 = 0.1 = k\,[2]^m\,[3]^n$

$R_2 = 0.9 = k\,[6]^m\,[3]^n$

$R_3 = 0.9 = k\,[6]^m\,[6]^n$

$$\frac{R_1}{R_2} = \left[\frac{2}{6}\right]^m \Rightarrow \frac{0.1}{0.9} = \left[\frac{1}{3}\right]^m \Rightarrow m = 2$$

$$\frac{R_2}{R_3} = \left[\frac{3}{6}\right]^n \Rightarrow \frac{0.9}{0.9} = \left[\frac{1}{2}\right]^n \Rightarrow n = 0$$

$\therefore$ $n = 0, m = 2$

$\therefore$ Rate = $k\,[A]^2$

8. It is due to improper orientation. Energy more than threshold energy and proper orientation are the two main factors which are responsible for a reaction to occur.

9. The overall rate of reaction depends upon the slowest step. Hence, the slowest step is called the rate determining step.

10. In elementary reaction (single step process) order and molecularity are same.

11. The representation of rate of reaction in terms of concentration of reactant is known as rate law.
Rate = $k.C^n$
where n is the order of a reaction and is determined experimentally.

12. $$-\frac{1}{4}\frac{d[NH_3]}{dt}=-\frac{1}{5}\frac{d[O_2]}{dt}=+\frac{1}{4}\frac{d[NO]}{dt}=+\frac{1}{6}\frac{d[H_2O]}{dt}$$

(a) Rate of disappearance of NH_3 = Rate of formation of NO
$= 3.6 \times 10^{-3}$ mol L^{-1} s^{-1}.

(b) Rate of formation of $H_2O = \frac{6}{4} \times$ Rate of formation of NO

$$=\frac{6}{4}\times 3.6\times 10^{-3}=5.4\times 10^{-3}\text{ mol L}^{-1}\text{ s}^{-1}$$

13. For first order reaction,

$$k=\frac{2.303}{t}\log\frac{[R]_0}{[R]}\text{, at } t_{1/2}, [R]=\frac{[R]_0}{2}$$

$$\therefore\quad k=\frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2}\text{ or, } t_{1/2}=\frac{2.303}{k}\log 2$$

$$t_{1/2}=\frac{2.303\times 0.3010}{k}\Rightarrow t_{1/2}=\frac{0.693}{k}$$

Thus for first order reaction, $t_{1/2}$ is independent of initial concentration.

14. The minimum energy required for a reactant molecule to form activated complex is called activation energy.
$E_a = E_T - E_R$
Activation energy is calculated by determining rate of a reaction at two different temperatures using Arrhenius equation.

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

15. The given reaction is

	$A_{(g)}$	$\rightarrow$	$B_{(g)}$	+	$C_{(g)}$	+	$D_{(g)}$
Initial pressure	P_o		0		0		0
After 20 min.	$P_o - x$		x		x		x

Total pressure = $P_o - x + x + x = P_o + 2x$

$$P_o+2x=P_o+P_o\times\frac{40}{100}\Rightarrow 2x=0.4P_o$$

$$\therefore\quad x=\frac{P_o}{5}$$

Now, $[R]_0 = P_o$

$$[R]=P_o-x=P_o-\frac{P_o}{5}=0.8\,P_o$$

Using formula, $k=\frac{2.303}{t}\log_{10}\frac{[R]_0}{[R]}$

or, $$k=\frac{2.303}{20\text{ min}}\log_{10}\frac{P_o}{0.8P_o}$$

or, $$k=\frac{2.303}{20\text{ min}}\log 1.25\quad\text{or,}\quad k=\frac{2.303\times 0.0969}{20\text{ min}}$$

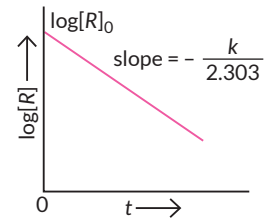
$k = 1.115 \times 10^{-2}$ min^{-1}

16. Rate of reaction increases by two fold when [A] is doubled. Hence, order of reaction w.r.t. A is one. Rate of reaction increases by four fold when [B] is doubled.
Hence, order of reaction *w.r.t. B* is two
i.e., Rate = $k[A][B]^2$
or, order of reaction = 1 + 2 = 3

OR

For first order reaction :

$$\log_{10}[R]=-\frac{k}{2.303}t+\log_{10}[R]_0$$



17. (a) The ratio of change of concentration and total time consumed in the change is called average rate.

$$r_{av.}=\frac{\Delta C}{\Delta t}$$

(b) A complex reaction proceeds through several elementary reactions. Numbers of molecules involved in each elementary reaction may be different *i.e.*, molecularity of each step may be different. Hence, we cannot talk about molecularity of overall reaction. The order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in case of complex reactions.

18. (i) (a) It considers atoms/molecules to be hard spheres and ignores their structural aspects.
(b) The molecules must collide with sufficient kinetic energy and in proper orientation.
(ii) A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
It increases the rate of reaction by decreasing the activation energy.

19. At 27 °C, $T_1 = 273 + 27 = 300$ K, $(t_{1/2})_1 = 30$ min
At 47 °C, $T_2 = 273 + 47 = 320$ K, $(t_{1/2})_2 = 10$ min

$$\therefore\quad k_2=\frac{0.693}{10\text{ min}}\text{ and }k_1=\frac{0.693}{30\text{ min}}$$

or, $\frac{k_2}{k_1}=\frac{0.693}{10\,\text{min}}\times\frac{30\,\text{min}}{0.693}=\frac{3}{1}$

Using Arrhenius equation,

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_2\times T_1}\right]$$

or, $\log\frac{3}{1}=\frac{E_a}{2.303R}\left[\frac{320-300}{320\times300}\right]$

or, $0.4771=\frac{E_a}{2.303\times8.314\,\text{J K}^{-1}\text{mol}^{-1}}\times\frac{20}{96000}$

or $E_a = 0.4771 \times 19.147\ \text{J K}^{-1}\ \text{mol}^{-1} \times 4800\ \text{K}$
$= 43848\ \text{J mol}^{-1} = 43.848\ \text{kJ mol}^{-1}$

20. Let initial concentration of the reactant = 100

Thus at t = 10 min, $a - x = 80$

t = ?, when $a - x = 25$

For a first order reaction

$$k=\frac{2.303}{10\,\text{min}}\log\frac{100}{80}=\frac{2.303}{10\,\text{min}}\log\frac{5}{4} \quad ...(i)$$

and $$k=\frac{2.303}{t}\log\frac{100}{25}=\frac{2.303}{t}\log 4 \quad ...(ii)$$

From eqn. (i) and (ii)

$$\frac{2.303}{10\,\text{min}}\log\frac{5}{4}=\frac{2.303}{t}\log 4 \text{ or } 0.0223\,\text{min}^{-1}=\frac{1.3865}{t}$$

$$t=\frac{1.3865}{0.0223}=62.2\,\text{min}$$

OR

The given data is

$$0.5\ \text{mol L}^{-1}\xrightarrow{5\ \text{min}}0.25\ \text{mol L}^{-1}\xrightarrow{5\ \text{min}}0.125\ \text{mol L}^{-1}$$

(i) Half life period is independent of initial concentration of the reactant, hence reaction is of first order.

(ii) For first order reaction

$$k=\frac{0.693}{t_{1/2}}=\frac{0.693}{5\,\text{min}}=0.138\,\text{min}^{-1}$$

21. (a) $(CH_3)_3COOC(CH_3)_3 \longrightarrow 2CH_3COCH_3 + C_2H_6$

$t = 0$	p_0	0	0
t	$p_0 - p$	$2p$	p

Total pressure at time t, $P_t = p_0 + 2p \Rightarrow p = \frac{P_t - p_0}{2}$

Pressure of C_2H_6 $(P) = \frac{P_t - P_0}{2}$

(b) The integrated expression,

$$kt = 2.303\log\frac{2p_0}{3p_0-p_t} \quad ...(i)$$

(c) $p_0 - p = 169.3 - 43.35 = 125.95$ Torr

$$k = \frac{2.303}{15}\log\frac{169.3}{125.95} = 0.0197\ \text{min}^{-1}$$

OR

From the given data at t = 0 and t = 15 min.,

$P_t = p_0 + 2p$

$256 = 169.3 + 2p$

$p = \frac{256-169.3}{2} = 43.35$ Torr

Pressure of $C_2H_6 = p = 43.55$ Torr

22. (i) The highly unstable transition state between reactants and products is called activated complex.

$$\underset{\text{Reactant}}{A+B} \rightarrow \underset{\substack{\text{Activated}\\\text{complex}}}{AB} \rightarrow \text{Product}$$

Energy of activation = Energy of activated complex
– Average energy of reactants.

(ii) Given that the rate of souring of milk at 20°C is three times as fast as at 3°C.

Therefore, $\frac{k_{(293\,\text{K})}}{k_{(276\,\text{K})}}=3,$

Since $\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

or $E_a=\frac{2.303RT_1T_2}{(T_2-T_1)}\log\frac{k_{293\,\text{K}}}{k_{276\,\text{K}}}$

$$=\frac{2.303\times8.314\times10^{-3}\times276\times293}{17}\log3 = 43.46\ \text{kJ mol}^{-1}$$

23. (i) Given : $k = 0.0030\ \text{mol L}^{-1}\ \text{s}^{-1}$, $n = 0$

$[R]_0 = 0.10$ M, $[R] = 0.075$ M

Using formula, $t=\frac{[R]_0-[R]}{k}=\frac{0.10\,\text{M}-0.075\,\text{M}}{0.0030\,\text{mol L}^{-1}\,\text{s}^{-1}}$

$$t=\frac{0.025}{0.0030}=8.3\,\text{s}$$

(ii) (a) For a first order reaction, $k=\frac{2.303}{t}\log\frac{[R]_0}{[R]}$

Given t = 15 min, $R = 0.8[R]_0$

or, $k=\frac{2.303}{15}\log\frac{[R]_0}{0.8[R]_0}$ or, $k=\frac{2.303}{15}\log\frac{10}{8}$ ... (i)

or, $k = 0.015\ \text{min}^{-1}$

(b) When $[R] = 0.1\,[R]_0$, t = ?

$$k=\frac{2.303}{t_1}\log\frac{[R]_0}{0.1[R]_0}=\frac{2.303}{t_1}\log 10 \quad ... (ii)$$

or, $0.015\,\text{min}^{-1}=\frac{2.303}{t_1}$ or, $t_1=\frac{2.303}{0.015\,\text{min}^{-1}}$

$t_1 = 153.53$ min

∴ After 153.53 min, 10% of the original material remains unreacted.

(c) Also, $k=\frac{2.303}{t_2}\log\frac{0.8[R]_0}{0.64[R]_0}=\frac{2.303}{t_2}\log\frac{10}{8}$ ...(iii)

From eq. (i) and eq. (iii),

$$\frac{2.303}{15}\log\frac{10}{8}=\frac{2.303}{t_2}\log\frac{10}{8}$$

∴ $t_2 = 15$ min

24. (i) Generally, rate of a chemical reaction increases with increase in temperature. It was found that for a chemical reaction with rise in temperature by 10°C, the rate constant is nearly doubled.

(ii) For a first order reaction $t_{1/2} = 0.693/k$

or $k = 0.693/t_{1/2}$

$$k = \frac{0.693}{10\,\text{min}} = 0.0693\,\text{min}^{-1} \simeq \frac{0.0693}{60}\text{s}^{-1} = 0.001155\,\text{s}^{-1}$$

Now from the Arrhenius equation $k = Ae^{-E_a/RT}$

or $\ln k = \ln A - \frac{E_a}{RT}$ or $\log k = \log A - \frac{E_a}{2.303RT}$

Substituting the given values, we get

$$\log 0.001155 = \log(4\times10^{13}) - \frac{98.6\times10^3}{2.303\times8.314\times T}$$

or $$-2.9374 = 13.6021 - \frac{5149.6}{T}$$

Hence, $$T = \frac{5149.6}{(13.6021+2.9374)}\,\text{K} = 311.35\ \text{K}$$

25. (i) A reaction in which rate is independent of concentration of reactants is called zero order reaction. *e.g.*, thermal decomposition of HI on gold surface.

(ii) The given rate law equation can be written as

$$-\frac{d[NH_3]}{dt} = \frac{k_1}{1/[NH_3]+k_2}$$

(a) If $[NH_3]$ is very high, $1/[NH_3]$ becomes negligible

$$\therefore\ -\frac{d[NH_3]}{dt} = \frac{k_1}{k_2} = k$$

i.e., rate becomes independent of concentration. Hence, it is of zero order.

(b) If $[NH_3]$ is very small, $1/[NH_3]$ will be very large ($>>k_2$), so that k_2 can be neglected in comparison to $1/[NH_3]$. Hence $-\frac{d[NH_3]}{dt} = \frac{k_1}{1/[NH_3]} = k_1[NH_3]$

Thus, reaction is of 1st order.

OR

(i) The reactions which are of second order but behave like first order reactions are called pseudo first order reactions *e.g.*, during hydrolysis of ethyl acetate (ester) with water, the concentration of water does not alter much during the reaction. So, in the rate equation, the rate of change in water concentration (the reactant which is in excess) can be taken as constant hence the reaction behaves as first order reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate = $k'[CH_3COOC_2H_5][H_2O]$ the term $[H_2O]$ can be taken as constant. Hence, the rate equation becomes

Rate = $k[CH_3COOC_2H_5]$ where $k = k'[H_2O]$.

(ii) Expression for rate constant of a zero order reaction is

$$k = \frac{[R]_0 - [R]}{t}$$

where $[R]_0$ is the initial concentration, $[R]$ is the final concentration and t is time.

k = proportionality constant called rate constant of reaction.

Unit of rate constant of zero order reaction.

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

x and y are zero for zero order reaction.

or k = mol L^{-1} s^{-1}

CHAPTER

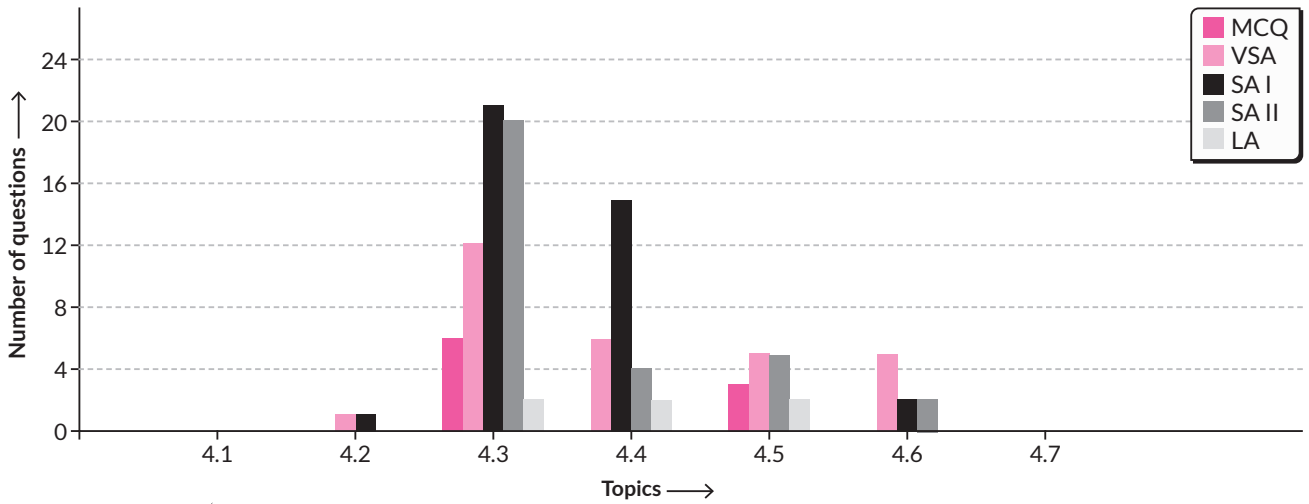
4

The *d*- and *f*- Block Elements

TOPICS

4.1 Position in the Periodic Table
4.2 Electronic Configurations of the *d*-Block Elements
4.3 General Properties of the Transition Elements (*d*-Block)
4.4 Some Important Compounds of Transition Elements
4.5 The Lanthanoids
4.6 The Actinoids
4.7 Some Applications of *d*-and *f*-Block Elements

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topic 4.3 and 4.4 are highly scoring topics.
- Maximum total weightage is of Topic 4.3 *General Properties of the Transition Elements (d-Block).*
- Maximum MCQ, VSA, SA I, SA II, LA type questions were asked from Topic 4.3 *General Properties of the Transition Elements (d-Block).*

QUICK RECAP

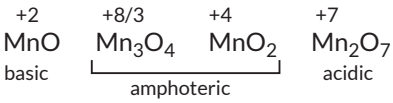
TRANSITION ELEMENTS (*d*-BLOCK ELEMENTS)

- Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements* or *d-block elements.*
- Their general electronic configuration is $(n-1)d^{1-10}ns^{0-2}$.
- **Transition series :** *d*-block consists of four transition series,
  1st Transition series or 3*d* series $_{21}Sc - _{30}Zn$
  2nd Transition series or 4*d* series $_{39}Y - _{48}Cd$
  3rd Transition series or 5*d* series $_{57}La$, $_{72}Hf - _{80}Hg$
  4th Transition series or 6*d* series $_{89}Ac$, $_{104}Rf - _{112}Cn$
- **General characteristics :**

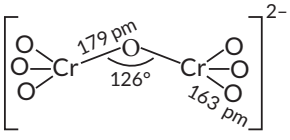
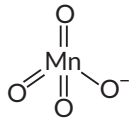
Melting and boiling points	High due to strong metallic bonding.
Enthalpies of atomisation	High due to strong interatomic interactions.

Ionisation enthalpies	Generally increases from left to right in a series.
Oxidation states	Variable due to participation of *ns* and $(n-1)d$ electrons.
Atomic radii	Decrease from left to right but become constant when pairing of electrons takes place.
Complex formation	Form complexes due to high nuclear charge, small size of metal ions and availability of empty *d*-orbitals to accept lone pair of electrons donated by ligands.
Coloured compounds	Form coloured compounds due to *d-d* transitions.
Magnetic properties	Transition metal ions and their compounds are paramagnetic due to presence of unpaired electrons in the $(n-1)d$-orbitals and it is calculated by using the formula, $\mu = \sqrt{n(n+2)}$ where, *n* is the no. of unpaired electrons.
Catalytic behaviour	Due to variable oxidation states and ability to form complexes.
Interstitial compounds	Due to empty spaces in their lattices, small atoms can be easily accommodated.
Alloy formation	Due to similar atomic sizes.

- Oxides in higher oxidation state of metal are acidic, in lower oxidation state are basic, whereas in the intermediate oxidation state are amphoteric.



- **Some important compounds :**

Compounds	Preparation	Properties	Uses
Potassium dichromate ($K_2Cr_2O_7$) 	From sodium dichromate (obtained from chromite ore) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	Orange red crystalline solid, oxidising agent having melting point 398°C. **Oxidising agent in acidic medium :** $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ **Oxidises :** I^- to I_2, H_2S to S, Sn^{2+} to Sn^{4+} and Fe^{2+} to Fe^{3+}	In dyeing, photography and leather industry.
Potassium permanganate ($KMnO_4$) 	From potassium manganate (obtained from pyrolusite) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$ $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$	Deep purple crystalline solid, oxidising agent, having melting point 240°C. **Oxidising agent in acidic medium :** $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ **Oxidises :** I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^- **Oxidising agent in faintly alkaline or neutral medium :** $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ **Oxidises :** I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2	As a disinfectant, germicide, and Baeyer's reagent (alkaline $KMnO_4$), it is also used in analytical chemistry.

- Volumetric titrations involving $KMnO_4$ are carried out only in the presence of dil. H_2SO_4 but not in the presence of HCl or HNO_3 because HCl is oxidised to Cl_2 and HNO_3 is itself a strong oxidising agent and partly oxidises the reducing agent. H_2SO_4 does not give any oxygen of its own to oxidise the reducing agent.

- In CrO_4^{2-} and CrO_4^- ion, Cr is present in +6 oxidation state and has d^0 configuration. Therefore, these ions should not be coloured but CrO_4^{2-} ion is yellow and CrO_4^- ion is orange. Their colour can be explained on the basis of charge transfer. There is momentary transfer of negative charge from O-atom to Cr-atom (O^{2-} ion changes momentary to O^- and oxidation state of Cr changes from +6 to +5.
- In MnO_4^- ion, Mn is present in +7 oxidation state and has d^0 configuration. MnO_4^- is purple/violet in colour due to charge transfer (negative charge from O-atom to Mn-atom).
- Chromyl chloride test : When $K_2Cr_2O_7$ is treated with a soluble chloride salt and concentrated sulphuric acid, reddish brown vapours of chromyl chloride (CrO_2Cl_2) are obtained.

USE OF TRANSITION METALS AND THEIR COMPOUNDS :

- Zn, Cd and Ni are used in the battery.
- $TiCl_4$ (Ziegler-Natta catalyst) is used in the manufacture of polythene.
- Fe + Mo are used as catalyst in manufacture of NH_3 by Haber's process.

INNER TRANSITION ELEMENTS (*f*-BLOCK ELEMENTS)

- **Lanthanoids :** Last electron enters one of the 4*f*-orbitals. Cerium (at. no. 58) to lutetium (at. no. 71).
- **Actinoids :** Last electron enters one of the 5*f*-orbitals. Thorium (at. no. 90) to lawrencium (at. no. 103).

General electronic configuration :
$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

General characteristics of lanthanoids :

Atomic and ionic radii	Decrease on going from La to Lu.
Oxidation states	Most common oxidation state of lanthanoids is +3. Some elements exhibit +2 and +4 oxidation states due to extra stability of empty, half-filled or fully-filled *f*-subshell, *e.g.*, Ce^{4+} acts as an oxidising agent and gets reduced to Ce^{3+}, Eu^{2+}, Yb^{2+} act as strong reducing agents and get oxidised to Eu^{3+} and Yb^{3+}.
Action of air	All the lanthanoids are silvery white soft metals and tarnish readily in moist air. They burn in oxygen of air and form oxides (Ln_2O_3 type).
Coloured ions	They form coloured trivalent metal ions due to *f-f* transitions of unpaired electrons. La^{3+} and Lu^{3+} are colourless ions due to empty ($4f^0$) or fully filled ($4f^{14}$) orbitals.
Magnetic properties	La^{3+}, Lu^{3+} are diamagnetic while trivalent ions of the rest of lanthanoids are paramagnetic.
Reducing agents	They readily lose electrons and are good reducing agents.
Electropositive character	Highly electropositive because of low ionisation energies.
Alloy formation	They form alloys easily with other metals especially iron.
Tendency to form complexes	Lanthanoids do not have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.

Lanthanoid contraction : In lanthanoid series, with increasing atomic number, there is progressive decrease in atomic/ionic radii (M^{3+} ions) from La^{3+} to Lu^{3+}.

- **Reason :** Due to addition of new electrons into *f*-subshell and imperfect shielding of one electron by another in the *f*-orbitals, there is greater effect of increased nuclear charge than screening effect hence contraction in size occurs.
- **Consequences :** Their separation is difficult, they have small differences in properties and 4*d* and 5*d* transition series have almost same atomic radii (Zr and Hf have similar properties due to same size).

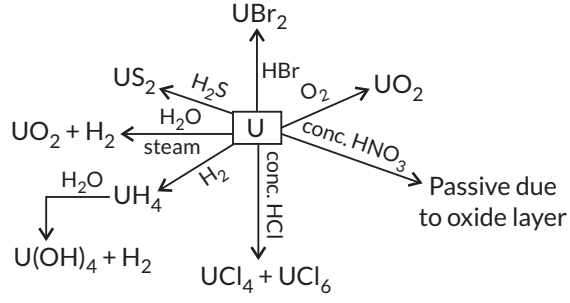
Uses of lanthanoids : Used in making mischmetal, an alloy of a lanthanoid metal (~ 95%) with iron (~ 5%) and traces of S, C, Ca and Al. It is used to make tracer bullets, shells and lighter flints.

General characteristics of actinoids :

Ionic radii	Like lanthanoids, ionic radii decrease across the series. Actinoid contraction is greater due to poor sheilding effect of the 5*f*-electrons. Further, 5*f*-orbitals extend in space beyond 6*s* and 6*p*-orbitals whereas 4*f*-orbitals are buried deep inside the atom.

Oxidation states	Like lanthanoids, most common oxidation state is +3. They also show oxidation state of +4, +5, +6 and +7, *e.g.*, in Th, Pa, U and Np respectively. They show a large number of oxidation states because of very small energy gap between 5*f*, 6*d* and 7*s* subshells.
Action of air, alkalies and acids	Like lanthanoids they are also silvery white metals, tarnish rapidly in air forming oxide coating and are not attacked by alkalies and are less reactive towards acids.
Coloured ions	Coloured due to *f-f* transition except $Ac^{3+}(5f^0)$, $Cm^{3+}(5f^7)$ and $Th^{4+}(5f^0)$ which are colourless.
Magnetic properties	They are strongly paramagnetic.
Density	All actinoids except thorium and americium have high densities.
Melting and boiling points	High melting and boiling points however there is no regular trend with rise in atomic number.
Ionisation energy	They have low ionisation energies than lanthanoides.
Reducing agents	All actinoids are strong reducing agents.
Electropositive character	Highly electropositive metals.

Chemical reactivity : Actinoids are highly reactive metals especially in the finely divided state. They reacts with boiling water to give a mixture of oxide and hydride.



Uses of actinoids : Thorium (Th) is used in atomic reactor and treatment of cancer. U and Pu are used as fuel in nuclear reactor.

Differences between lanthanoids and actinoids :

Lanthanoids	Actinoids
They show +2 and +4 oxidation states in few cases besides +3.	They show higher oxidation states of +4, +5, +6 and +7 besides +3.
Except promethium, they are non-radioactive.	All actinoids are radioactive.
They do not form oxo-cations.	They form oxo-cations like UO_2^{2+}, PuO_2^{2+}, UO_2^{+}, etc.
The compounds of lanthanoids are less basic.	Actinoid compounds are more basic.
They have less tendency of complex formation.	They have greater tendency of complex formation.

THE *d*- AND *f*- BLOCK ELEMENTS

The *d*-Block Elements

Transition elements
$(n-1)d^{1-10}\ ns^{0-2}$

Classification

Series	Elements
First transition or 3*d*-series	Sc (Z = 21) to Zn (Z = 30)
Second transition or 4*d*-series	Y (Z = 39) to Cd (Z = 48)
Third transition or 5*d*-series	La (Z = 57), Hf (Z = 72) to Hg (Z = 80)
Fourth transition or 6*d*-series	Ac (Z = 89), Rf (Z = 104) to Cn (Z = 112)

Properties

- **Atomic radii :** In I, II, III series → first decrease and then remains same. Atomic radii of III transition series = II transition series > I transition series (due to lanthanoid contraction.)
- **Oxidation states** → variable.
- **M.P. and B.P.** → rise to max. and then decrease.
  W → high M.P. (3414°C).
- **Ionisation energies :** In periods → increases. In groups → decreases from I member to II, increases from II to III member.
- Mostly coloured due to excitation of *d*-electrons.
- Show catalytic property.
- Form interstitial compounds.

Important Compounds of *d*-Block Elements

	Preparation	Properties	Uses
Potassium dichromate ($K_2Cr_2O_7$)	From sodium dichromate: $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$	• Orange crystalline solid, melting point = 669 K. • Moderately soluble in cold water but freely soluble in hot water. • Powerful oxidising agent.	• In chrome tanning in leather industry. • In calico printing and dyeing. • In photography and in hardening gelatine film.
Potassium permanganate ($KMnO_4$)	From potassium manganate: $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$	• Deep purple, melting point = 513 K. • Moderately soluble in water at room temperature and more soluble in hot water. • Powerful oxidising agent.	• Baeyer's reagent (alkaline $KMnO_4$) to test unsaturation in organic compounds. • As a disinfectant and germicide. • For bleaching of wool, cotton, silk and other textile fibres and also for decolourisation of oils.

The *f*-Block Elements

Inner transition elements
$(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$

Classification

Series	Elements
Lanthanides or 4*f*-series	Ce (Z = 58) to Lu (Z = 71)
Actinides or 5*f*-series	Th (Z = 90) to Lr (Z = 103)

Trends and Characteristics of Actinides

- All actinides show +3 oxidation state.
- They are highly reactive metals.
- All the metals are radioactive.
- They are generally coloured [except $Ac^{3+}(5f^0)$, $Cm^{3+}(5f^7)$ and $Lr^{3+}(5f^{14})$ are colourless].

Trends and Characteristics of Lanthanides

- Show common stable oxidation state +3.
- Regular decrease in atomic and ionic radii with increase in atomic number is called lanthanide contraction.
- They have low *I.E.* and high b.pt. and m.pt.
- They form coloured compounds due to *f*-*f* transitions.
  $La^{3+}(4f^0)$, $Gd^{3+}(4f^7)$, $Lu^{3+}(4f^{14})$ → Colourless
  $Ce^{3+}(4f^1)$ and $Yb^{3+}(4f^{13})$ → Colourless despite of having unpaired electrons (exceptions).

BRAIN MAP

Previous Years' CBSE Board Questions

4.2 Electronic Configurations of the *d*-Block Elements

VSA (1 mark)

1. Account for the following :
Zn, Cd, Hg are considered as *d*-block elements but not as transition elements. *(1/5, 2020)*

OR

Account for the following :
Zn is not considered as a transition element.
(1/5, AI 2014) U

SA I (2 marks)

2. What are the transition elements? Write two characteristics of the transition elements.
(Term II, 2021-22C, Delhi 2015)

4.3 General Properties of the Transition Elements (*d*-Block)

MCQ

3. Which property of transition metals enables them to behave as catalysts?
(a) High melting point
(b) High ionisation enthalpy
(c) Alloy formation
(d) Variable oxidation states *(2023)*

4. Which of the following is a strong oxidising agent?
(At. No. Mn = 25, Zn = 30, Cr = 24, Sc = 21)
(a) Mn^{3+} (b) Zn^{2+} (c) Cr^{3+} (d) Sc^{3+}
(2021 C)

5. The incorrect statement about interstitial compounds is
(a) they are chemically reactive.
(b) they are very hard.
(c) they retain metallic conductivity.
(d) they have high melting point. *(2020)* R

6. Out of the following transition elements, the maximum number of oxidation states are shown by
(a) Sc (Z = 21) (b) Cr (Z = 24)
(c) Mn (Z = 25) (d) Fe (Z = 26) *(2020)*

7. **Assertion (A) :** Transition metals have high melting point.
Reason (R) : Transition metals have completely filled *d*-orbitals.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

8. **Assertion (A) :** Transition metals have low melting points.
Reason (R) : The involvement of greater number of $(n-1)d$ and ns electrons in the interatomic metallic bonding.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)* U

VSA (1 mark)

Read the given passage and answer the questions number (9 to 13) that follow :

The *d*-block of the periodic table contains the elements of groups 3-12 and are known as transition elements. In general, the electronic configuration of these elements is $(n-1)d^{1-10}\,ns^{1-2}$. The *d*-orbitals of the penultimate energy level in their atoms receive electrons giving rise to three rows of the transition metals *i.e.*, 3*d*, 4*d* and 5*d* series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation states, complex formation, formation of coloured ions and alloys, catalytic activity, etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

9. Why are Zn, Cd and Hg non-transition elements?

10. Which transition metal of 3*d* series does not show variable oxidation states?

11. Why do transition metals and their compounds show catalytic activity?

12. Why are melting points of transition metals high?

13. Why is Cu^{2+} ion coloured while Zn^{2+} ion is colourless in aqueous solution? *(2020)*

14. Out of zinc and tin, whose coating is better to protect iron objects? *(One word, 2020)*

15. Account for the following :
Copper(I) compounds are white whereas copper(II) compounds are coloured. *(1/5, 2020)* Ap

16. Write the formula of an oxoanion of chromium (Cr) in which it shows the oxidation state equal to its group number. *(NCERT, Delhi 2017)*

17. Write the formula of an oxoanion of manganese (Mn) in which it shows the oxidation state equal to its group number. *(Delhi 2017)*

18. How would you account for the following :
Transition metals form coloured compounds?
(1/3, Delhi 2015)

19. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why? *(AI 2015)* U

20. Why do transition elements show variable oxidation states? *(Delhi 2014C)*

SA I (2 marks)

21. Calculate the spin-only moment of Co^{2+} ($Z = 27$) by writing the electronic configuration of Co and Co^{2+}. *(2/5, 2020)*

22. Give reason and select one atom/ion which will exhibit asked property :
(i) Sc^{3+} or Cr^{3+} (exhibit diamagnetic behaviour)
(ii) Cr or Cu (high melting and boiling point)
(2/5, 2020) An

23. Calculate the number of unpaired electrons in the following gaseous ions :
Mn^{3+} and Cr^{3+} (Atomic number of Cr = 24, Mn = 25)
Which one of them is most stable in aqueous solution and why ? *(2020 C)*

24. Calculate the number of unpaired electrons in the following gaseous ions :
Ti^{3+} and Cr^{3+} (Atomic number of Ti = 22, Cr = 24)
Which one of them is most stable in aqueous solution and why ? *(2020 C)*

25. Give reasons for the following :
(i) Transition metals form alloys.
(ii) Mn_2O_3 is basic whereas Mn_2O_7 is acidic.
(2/3, Delhi 2019)

26. Use the data to answer the following and also justify giving reasons :

	Cr	Mn	Fe	Co
$E^\circ_{M^{2+}/M}$	−0.91	−1.18	−0.44	−0.28
$E^\circ_{M^{3+}/M^{2+}}$	−0.41	+1.57	+0.77	+1.97

(i) Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?
(ii) Which is the most stable ion in +2 oxidation state and why? *(AI 2019)*

27. Give reasons :
(a) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.
(b) The d^1 configuration is very unstable in ions.
(2019 C)

28. (i) How is the variability in oxidation states of transition metals different from that of the *p*-block elements?
(ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why? *(2/5, Delhi 2017)*

29. Account for the following :
(i) Transition metals show variable oxidation states.
(ii) Zn, Cd and Hg are soft metals. *(2/5, AI 2017)*

30. Give reasons :
(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
(ii) Transition metals show variable oxidation states.
(2/3, Delhi 2016) U

31. Account for the following :
(i) Transition metals show variable oxidation states.
(ii) Cu^+ ion is unstable in aqueous solution.
(2/3, AI 2015)

32. Why do transition elements show variable oxidation states? In 3*d* series (Sc to Zn), which element shows the maximum number of oxidation states and why?
(Foreign 2015)

33. How would you account for the following :
(i) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7.
(ii) Transition metals and their compounds show catalytic properties. *(2/3, Foreign 2015)*

34. What is meant by 'disproportionation'? Give an example of a disproportionation reaction in aqueous solution. *(NCERT)*
(Delhi 2015C, AI 2015C)

35. Account for the following :
(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
(ii) The enthalpy of atomization is lowest for Zn in 3*d* series of the transition elements. *(Delhi 2014)*

36. (i) Write two characteristic of the transition elements.
(ii) Which of the 3*d*-block elements may not be regarded as the transition elements and why?
(2/3, Foreign 2014)

37. Assign a reason for each of the following observations :
(i) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
(ii) The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly. *(Delhi 2014C)*

38. Assign reasons for the following :
(i) Copper(I) ion is not known to exist in aqueous solutions.
(ii) Both O_2 and F_2 stabilize high oxidation states of transition metals but the ability of oxygen to do so exceeds that of fluorine. *(AI 2014C)*

39. Give reasons for the following :
(i) Transition metals exhibit a wide range oxidation states.
(ii) Cobalt (II) is very stable in aqueous solutions but gets easily oxidised in the presence of strong ligands. *(2/3, AI 2014C)*

40. Assign reasons for the following :
(i) Cu(I) ion is not known to exist in aqueous solutions. *(NCERT)* U
(ii) Transition metals are much harder than the alkali metals. *(2/3, AI 2014C)*

41. Assign reasons for the following :
(i) Transition metals and many of their compounds act as good catalysts.
(ii) Transition metals generally form coloured compounds. *(AI 2014C)*

SA II (3 marks)

42. Following are the transition metal ions of 3*d* series :
Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}
(Atomic numbers : Ti = 22, V = 23, Mn = 25, Cr = 24)
Answer the following :
(i) Which ion is most stable in aqueous solution and why?
(ii) Which ion is strong oxidising agent and why?
(iii) Which ion is colourless and why?
(Term II, 2021-22, 3/5, AI 2017)

43.

	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^\circ_{M^{2+}/M}$	– 0·91	– 1·18	– 0·44	– 0·28	– 0·25	+ 0·34	– 0·76

From the given E° values of the first row transition elements, answer the following questions :
(i) Why is $E^\circ_{Mn^{2+}/Mn}$ value highly negative as compared to other elements ?
(ii) What is the reason for the irregularity in the above E° values ?
(iii) Why is $E^\circ_{Cu^{2+}/Cu}$ value exceptionally positive ?
(Term II, 2021-22)

44. Account for the following
(i) Cu^{2+} salts are coloured while Zn^{2+} salts are white.
(ii) E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}
(iii) Transition metals form alloys. *(Term II, 2021-22)*

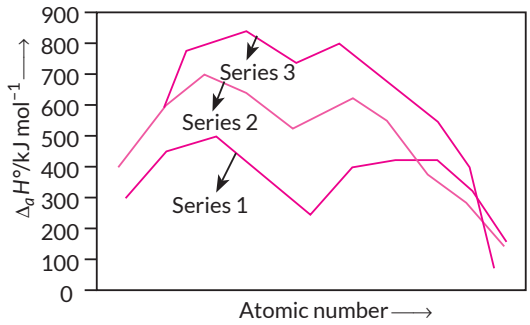
45. (i) Which ion amongst the following is colourless and why?
Ti^{4+}, Cr^{3+}, V^{3+}
(Atomic number of Ti = 22, Cr = 24, V = 23)
(ii) Why is Mn^{2+} much more resistant than Fe^{2+} towards oxidation?
(iii) Highest oxidation state of a metal is shown in its oxide or fluoride only. Justify the statement.
(Term II, 2021-22) Ap

46. (i) Silver atom has completely filled *d*-orbitals in its ground state, it is still considered to be a transition element. Justify the statement.
(ii) Why are $E^\circ_{M^{2+}/M}$ values of Mn and Zn more negative than expected?
(iii) Why do transition metals form alloys?
(Term II, 2021-22) An

47. Give reasons for the following statements :
(a) Copper does not displace hydrogen from acids. *(NCERT)*
(b) Transition metals and most of their compounds show paramagnetic behaviour.
(c) Zn, Cd and Hg are soft metals. *(Term II, 2021-22)*

48. (i) Why are melting points of transition metals high ?
(ii) Why the transition metals generally form coloured compounds ?
(iii) Why E° value for Mn^{3+}/Mn^{2+} couple is highly positive ? *(Term II, 2021-22)*

49. Answer the following questions on the basis of the figure given below :



(i) Which element in 3*d* series has lowest enthalpy of atomisation?
(ii) Why do metals of the second and third series have greater enthalpies of atomisation?
(iii) Why are enthalpies of atomisation of transition metals quite high? *(Term II, 2021-22)* Ap

50. Define transition metals. Why Zn, Cd and Hg are not called transition metals ? How is the variability in oxidation states of transition metals different from that of *p*-block elements ? *(Term II, 2021-22)*

51. Give reasons for the following statements :
(a) Transition elements and their compounds act as good catalysts.
(b) $E^\circ_{(Mn^{2+}/Mn)}$ value is highly negative as compared to other elements.
(c) Cr^{2+} is a strong reducing agent. *(Term II, 2021-22)*

52. Account for the following :
(a) Transition elements show variable oxidation states.
(b) $E^\circ_{Cu^{2+}/Cu}$ value for copper is highly positive.
(c) Cr^{2+} is a strong reducing agent.
(Term-II, 2021-22C)

53. Define transition elements. Write two characteristics of transition elements. *(Term-II, 2021-22C)*

54. (a) Why is $E^\circ(Cu^{2+}|Cu)$ exceptionally positive ? Although Cu^+ ion has $3d^{10}$ configuration, yet it is unstable in an aqueous solution. Why? What is the reason for the stability of Cu^{2+} over Cu^+ ion? *(2021C)*

55. Give reasons for the following:
(i) Transition metals form alloys.
(ii) Zinc has lowest enthalpy of atomization.
(iii) Managanese shows higher oxidation state of +4 with fluorine but shows +7 with oxygen. *(2021 C)*

56. Following ions are given :
Cr^{2+}, Cu^{2+}, Cu^{+}, Fe^{2+}, Fe^{3+}, Mn^{3+}
Identify the ion which is
(i) a strong reducing agent.
(ii) unstable in aqueous solution.
(iii) a strong oxidising agent.
Give suitable reason in each. *(2020)*

57. Give reasons :
(i) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.
(ii) Iron has higher enthalpy of atomization than that of copper.
(iii) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. *(2018)* Ap

58. Account the following :
(i) Transition metals form large number of complex compounds.
(ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.
(iii) E° value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}.
(3/5, Delhi 2017)

59. Account for the following :
(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of +4.
(ii) Cr^{2+} is a strong reducing agent.
(iii) Cu^{2+} salts are coloured, while Zn^{2+} salts are white. *(3/5, AI 2016)*

60.

$E^\circ_{(M^{2+}/M)}$	Cr	Mn	Fe	Co	Ni	Cu
	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34

From the given data of E° values, answer the following questions :
(i) Why is $E^\circ_{(Cu^{2+}/Cu)}$ value exceptionally positive?
(ii) Why is $E^\circ_{(Mn^{2+}/Mn)}$ value highly negative as compared to other elements?
(iii) Which is a stronger reducing agent Cr^{2+} or Fe^{2+}? Give reason. *(NCERT, 3/5, AI 2015)* An

61. Assign suitable reasons for the following :
(i) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.
(ii) In the 3*d* series from Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomization of Zn is the lowest.
(NCERT)
(iii) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. *(Foreign 2014)*

LA (5 marks)

62. Assign reason for each of the following :
(i) Manganese exhibits the highest oxidation state of +7 among the 3*d* series of transition elements.
(ii) Transition metals and their compounds are generally found to be good catalysts in chemical reactions.
(iii) Cr^{2+} is reducing in nature while with the same *d*-orbital configuration (d^4) Mn^{3+} is an oxidising agent.
(iv) Zn has lowest enthalpy of atomization.
(v) Cu^{+} is unstable in an aqueous solution. *(2023)*

63. The elements of 3*d* transition series are given as
Sc Ti V Cr Mn Fe Co Ni Cu Zn
Answer the following :
(i) Write the element which shows maximum number of oxidation states. Given reason.
(ii) Which element has the highest melting point?
(iii) Which element shows only +3 oxidation state?
(iv) Which element is a strong oxidising agent in +3 oxidation state and why? *(AI 2016)*

4.4 Some Important Compounds of Transition Elements

VSA (1 mark)

64. Account for the following :
Chromates change their colour when kept in an acidic solution. *(1/5, 2020)*

65. Complete the following equation :
$3MnO_4^{2-} + 4H^+ \longrightarrow$
(2020, 2019C 1/3, Foreign 2015)

66. Complete the following equation :
$2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow$
(2019C, 1/2, Delhi 2015)

67. Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?
(1/5, Delhi 2017) U

68. Complete the following equation :
$MnO_4^- + 8H^+ + 5e^- \longrightarrow$ *(1/5, Delhi 2014)*

69. Complete the following chemical equation:
$SO_2 + MnO_4^- + H_2O \longrightarrow$ *(1/2, AI 2014C)*

SA I (2 marks)

70. How would you account for
(a) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.
(b) Complete the following equation :
$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow$ *(2023)*

71. Complete the following equations :
(a) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow$
(b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow$ *(2023)*

72. Write the balanced chemical equations involved in the preparation of $KMnO_4$ from pyrolusite ore (MnO_2). *(2020)*

73. Write the balanced ionic equations showing the oxidising action of acidified dichromate ($Cr_2O_7^{2-}$) solutions with (i) iron (II) ion and (ii) tin (II) ion. *(2020)*

74. How do you prepare :
(i) K_2MnO_4 from MnO_2?
(ii) $Na_2Cr_2O_7$ from Na_2CrO_4? *(2020, 2/5, Delhi 2014)*

75. Explain all the steps along with the chemical equation which are used in the preparation of $K_2Cr_2O_7$ from chromite ore. *(2020 C)*

76. When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidizing agent, it gives a dark green compound (*A*). Compound (*A*) disproportionates in acidic solution to give purple compound (*B*). An alkaline solution of compound (*B*) oxidises KI to compound (*C*) whereas an acidified solution of compound (*B*) oxidises KI to (*D*). Identify (*A*), (*B*), (*C*) and (*D*). *(NCERT, Delhi 2019)* An

77. Complete and balance the following chemical equations :
(i) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow$
(ii) $MnO_4^- + H_2O + I^- \longrightarrow$ *(2018)* Ap

78. Complete the following equations :
(i) $2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow$
(ii) $KMnO_4 \xrightarrow{\text{Heat}}$ *(2/5, AI 2017)*

79. When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow coloured compound (*A*) is obtained which on acidification with dilute sulphuric acid gives a compound (*B*). Compound (*B*) on reaction with KCl forms an orange coloured crystalline compound (*C*).
(i) Write the formulae of the compounds (*A*), (*B*) and (*C*).
(ii) Write one use of compound (*C*). *(Delhi 2016)*

80. Complete the following chemical equations :
(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow$
(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow$ *(Delhi 2016)*

81. Complete the following equations.
(i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$
(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$ *(2/5, AI 2016)*

82. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (i) an iodide (ii) H_2S. *(AI 2015C)*

83. Complete the following equations :
(i) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$
(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow$ *(AI 2014)*

84. Complete the following equations :
(i) $2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow$
(ii) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$ *(Foreign 2014)*

SA II (3 marks)

85. What is the effect of pH on the solution of $K_2Cr_2O_7$? Also give the structure of chromate and dichromate ion along with the colour of species. *(2020 C)*

86. Explain the method of preparation of sodium dichromate from chromite ore. Give the equation representing oxidation of ferrous salts by dichromate ion. *(AI 2019)*

87. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (*A*). Compound (*A*) on acidification gives compound (*B*). Compound (*B*) on reaction with KCl forms an orange coloured compound (*C*). An acidified solution of compound (*C*) oxidises Na_2SO_3 to (*D*). Identify (*A*), (*B*), (*C*) and (*D*). *(2019)*

88. Complete the following reactions.
(i) $MnO_2 + KOH + O_2 \longrightarrow$
(ii) $I^- + MnO_4^- + H^+ \longrightarrow$
(iii) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow$ *(AI 2019)*

LA (5 marks)

89. (a) Account for the following :
(i) Manganese shows maximum number of oxidation states in 3d series.
(ii) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.
(iii) Ti^{4+} is colourless whereas V^{4+} is coloured in an aqueous solution.
(b) Write the chemical equations for the preparation of $KMnO_4$ from MnO_2. Why does purple colour of acidified permanganate solution decolourise when it oxidises Fe^{2+} to Fe^{3+}? *(2019)*

90. (a) Complete the following chemical reactions :
(i) $Na_2Cr_2O_7 + KCl \rightarrow$
(ii) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow$
(b) How does the colour of $Cr_2O_7^{2-}$ change when treated with an alkali? *(2019C)*

4.5 The Lanthanoids

MCQ

91. Lanthanoid contraction is due to increase in
(a) atomic number
(b) shielding by 4*f* electrons
(c) effective nuclear charge
(d) atomic radius. *(2023)*

92. The most common and stable oxidation state of a Lanthanoid is
(a) +2 (b) +3
(c) +4 (d) +6 *(2023)*

93. All the lanthanoids show + 3 as the common oxidation state, yet Ce shows + 4 state because
(a) it has a tendency to attain noble gas configuration.
(b) it has a variable ionization enthalpy.
(c) it has a tendency to gain 1 more electron.
(d) it has an unpaired electron in 6s. *(2020C)*

VSA (1 mark)

94. Give reasons for the following :
Eu^{2+} is a strong reducing agent. *(1/3, Delhi 2019)*

95. Account for the following :
Zr and Hf have almost similar atomic radii.
(1/5, AI 2015) U

96. Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.
(1/5, Delhi 2014)

97. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. *(1/5, AI 2014)*

98. What are the different oxidation states exhibited by the lanthanoids? *(1/3, Foreign 2014)*

SA II (3 marks)

99. (a) Write any two consequences of lanthanoid contraction.
(b) Name the element of 3*d* series which exhibits the largest number of oxidation states. Give reason.
(Term II, 2021-22)

100. Account for the following:
(i) Transition elements have higher enthalpies of atomisation.
(ii) Separation of a mixture of Lanthanoid elements is difficult.
(iii) The $E°_{M^{2+}/M}$ value for copper is positive.
(Term II, 2021-22)

101. (i) Which is the most common oxidation state in Lanthanoids ?
(ii) Why is there a gradual decrease in the atomic sizes of transition metals in a series with increasing atomic numbers ?
(iii) Calculate the number of unpaired electrons in the following gaseous ions :
V^{3+}, Ti^{3+} *(Term II, 2021-22C)*

102. (i) The electronic configuration of Ce is :
$_{58}Ce = [Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$
Calculate the spin only magnetic moment of Ce^{3+} ion.
(ii) Why is copper regarded as a transition element although copper atom has completely filled *d*-orbitals in its ground state ?
(iii) Why is Sc^{3+} colourless in aqueous solution whereas Ti^{3+} is coloured ? *(Term II, 2021-22C)*

103. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?
(Delhi 2015C)

LA (5 marks)

104. (a) (i) Write the number of unpaired electrons in Cr^{3+}. (Atomic number of Cr = 24)
(ii) Complete the reaction mentioning all the products formed:
$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow$
(b) Account for the following:
(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
(ii) Copper has exceptionally positive $E°_{M^{2+}/M}$ value.
(iii) Eu^{2+} with electronic configuration [Xe] $4f^7\ 6s^2$ is a strong reducing agent. *(2023)*

105. (a) Give reasons :
(i) Transition metals and their compounds show catalytic activities.
(ii) Separation of a mixture of Lanthanoid elements is difficult.
(iii) Zn, Cd and Hg are soft and have low melting points.
(b) Write the preparation of the following :
(i) $Na_2Cr_2O_7$ from Na_2CrO_4
(ii) K_2MnO_4 from MnO_2 *(2020)* Ap

4.6 The Actinoids

VSA (1 mark)

106. Give reasons :
Actinoids show irregularities in their electronic configurations. *(1/3, 2019, 1/3, Delhi 2016)*

107. How would you account for the following :
Actinoid contraction is greater than lanthanoid contraction? *(2019 C, 1/3, Delhi 2015)*

OR

Assign reasons for the following :
From element to element actinoid contraction is greater than the lanthanoid contraction.
(1/3, AI 2014C)

108. Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.
(1/5, Delhi 2017) R

109. Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons. *(1/5, Delhi 2017)*

110. Give reasons for the following :
Actinoids exhibit a greater range of oxidation states than lanthanoids. *(1/3, AI 2014C)*

SA I (2 marks)

111. Why do actinoids show a wide range of oxidation states? Write one similarity between the chemistry of lanthanoids and actinoids. *(2/5, AI 2015)*

112. With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids. *(2/5, AI 2014)*

SA II (3 marks)

113. Give three points of difference between lanthanoids and actinoids. *(3/5, 2020)*

114. Answer the following :
(a) What is the general electronic configuration of lanthanoids ?
(b) What are the common oxidation states of Cerium (At. no. 58) ?
(c) Why do actinoids show a wide range of oxidation states ? *(2019)*

CBSE Sample Questions

4.2 Electronic Configurations of the *d*-Block Elements

MCQ

1. Which of the following is the reason for zinc not exhibiting variable oxidation states?
   (a) Inert pair effect
   (b) Completely filled 3*d* subshell
   (c) Completely filled 4*s* subshell
   (d) Common ion effect *(2020-21)*

4.3 General Properties of the Transition Elements (*d*-Block)

MCQ

2. Which set of ions exhibit specific colours? (Atomic number of Sc = 21, Ti = 22, V=23, Mn = 25, Fe = 26, Ni = 28, Cu = 29 and Zn =30)
   (a) $Sc^{3+}, Ti^{4+}, Mn^{3+}$ (b) $Sc^{3+}, Zn^{2+}, Ni^{2+}$
   (c) V^{3+}, V^{2+}, Fe^{3+} (d) $Ti^{3+}, Ti^{4+}, Ni^{2+}$
   (2020-21)

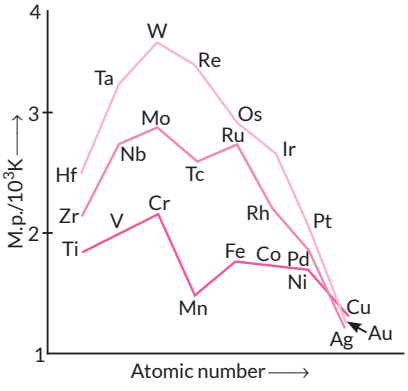
3. Which of the following is a diamagnetic ion? (Atomic numbers of Sc, V, Mn and Cu are 21, 23, 25 and 29 respectively.)
   (a) V^{2+} (b) Sc^{3+}
   (c) Cu^{2+} (d) Mn^{3+}
   (2020-21)

SA II (3 marks)

4. (a) Why are fluorides of transition metals more stable in their higher oxidation state as compared to the lower oxidation state?
   (b) Which one of the following would feel attraction when placed in magnetic field: $Co^{2+}, Ag^{+}, Ti^{4+}, Zn^{2+}$
   (c) It has been observed that first ionisation energy of 5*d* series of transition elements are higher than that of 3*d* and 4*d* series, explain why?

   OR

   On the basis of the figure given below, answer the following questions :



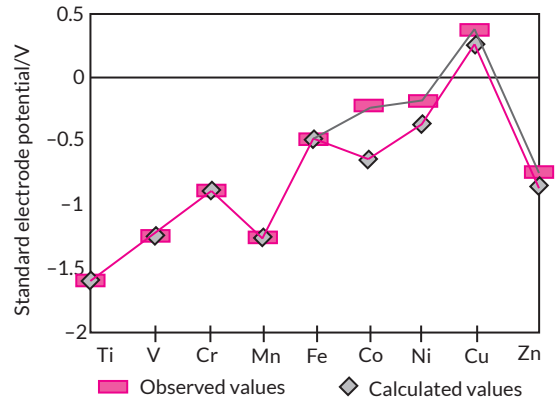
   (a) Why manganese has lower melting point than chromium?
   (b) Why do transition metals of 3*d* series have lower melting points as compared to 4*d* series?
   (c) In the third transition series, identify and name the metal with the highest melting point.
   (Term II, 2021-22) An

5. Account for the following :
   (a) Ti(IV) is more stable than the Ti(II) or Ti(III).
   (b) In case of transition elements, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number.
   (c) Zinc is comparatively a soft metal, iron and chromium are typically hard.
   (Term II, 2021-22)

6. Give reasons for the following :
   (i) Transition elements act as catalysts.
   (ii) It is difficult to obtain oxidation state greater than two for copper.
   (iii) $Cr_2O_7^{2-}$ is a strong oxidising agent in acidic medium whereas WO_3 and MoO_3 are not,

   OR

   Observed and calculated values for the standard electrode potentials of elements from Ti to Zn in the first reactivity series are depicted in the given figure:



   Explain the following observations :
   (i) The general trend towards less negative $E°$ values across the series.
   (ii) The unique behaviour of copper.
   (iii) More negative $E°$ values of Mn and Zn.
   (2020-21) U

4.4 Some Important Compounds of Transition Elements

MCQ

7. $KMnO_4$ is coloured due to
   (a) *d-d* transitions

(b) charge transfer from ligand to metal
(c) unpaired electrons in *d* orbital of Mn
(d) charge transfer from metal to ligand.
(*Term II, 2021-22*)

LA (5 marks)

8. Answer the following:
(a) Why are all copper halides known except that copper iodide?
(b) Why is the $E^{\circ}_{(V^{3+}/V^{2+})}$ value for vanadium comparatively low?
(c) Why HCl should not be used for potassium permanganate titrations?
(d) Explain the observation, at the end of each period, there is a slight increase in the atomic radius of *d*-block elements.
(e) What is the effect of pH on dichromate ion solution? (*Term II, 2021-22*)

4.6 The Actinoids

MCQ

9. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Magnetic moment values of actinides are lesser than the theoretically predicted values.
Reason (R) : Actinide elements are strongly paramagnetic.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. (*Term II, 2021-22*)

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. Zn, Cd, Hg are considered as *d*-block elements but not as transition elements because they do not have partly filled *d*-orbitals in their atomic state or their common oxidation states (*i.e.*, Zn^{2+}, Cd^{2+}, Hg^{2+}).

Key Points
- The electronic configuration of the elements should be well known.

2. Elements which have incompletely filled *d*-orbitals in their ground state or in any one of their oxidation states are called transition elements.
Characteristics of transition elements :
(i) They show variable oxidation states.
(ii) They exhibit catalytic properties.

3. **(d):** Due to variable oxidation states of transition metals, they show their catalytic activity.

4. Mn^{3+} is a strong oxidising agent having E° = +1.57 V.

5. **(a):** Interstitial compounds are chemically inert.

6. **(c)**

Key Points
- In 3*d* series, Mn has maximum number of oxidation state because number of unpaired electrons is maximum in Mn ($3d^5, 4s^2$).

7. **(c):** Because of strong metallic bonding present in atoms of transition elements, they have high melting points.

8. **(d):** Transition metals have high melting points because of the involvement of greater number of $(n-1)d$ and *ns* electrons in the interatomic metallic bonding.

9. Zn, Cd and Hg do not have partly filled *d*-orbital in their ground state or common oxidation state.

10. Scandium (Sc) exhibits only (+3) oxidation state.

11. The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. For example; vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation).

12. Strong metallic bonds between the atoms of transition elements are responsible for the high melting points.

13. Zn^{2+} ion has completely filled *d*-subshell and no *d-d* transition is possible. So zinc salts are colourless.

Configuration of Cu^{2+} is [Ar] $3d^9$. It has partly filled *d*-subshell and hence it is coloured due to *d-d* transition.

14. Zinc

15. Cu(I) compounds have completely filled *d*-orbitals and there are no vacant *d*-orbitals for promotion of electrons whereas Cu(II) compounds have one unpaired electron which is responsible for colour formation.

Concept Applied
- *d-d* transition is responsible for the colour formation of transition elements.

16. Oxoanion of chromium in which it shows +6 oxidation state equal to its group number is $Cr_2O_7^{2-}$ (dichromate ion).

17. Formula of oxoanion of manganese is MnO_4^-.
Oxidation state of Mn in this oxoanion = + 7
Group number of Mn is 7.

18. Due to presence of vacant *d*-orbitals and *d-d* transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

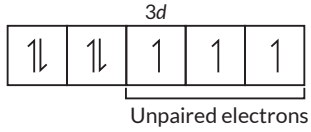
19. Zn^{2+} ion has completely filled *d*-subshell but Cu^{2+} ion has partly filled *d*-subshell.

20. Transition elements can use their *ns* and $(n-1)$ *d*-orbital electrons for bond formation therefore, they show variable oxidation states. Because, the energy difference between $(n-1)d$ orbital and *ns* orbital is small.

21. (b): Co = $[Ar]3d^7 4s^2$

$Co^{2+} = [Ar]3d^7$

$\therefore$



i.e., there are three unpaired electrons ($n = 3$).

Hence, $\mu = \sqrt{n(n+2)}$ B.M.

$= \sqrt{3(3+2)} = 3.87$ B.M.

22. (i) Sc^{3+} has $3d^0$ outer electronic configuration, therefore it is diamagnetic in nature whereas Cr^{3+} has $3d^3$ outer electronic configuration. So, it is paramagnetic due to presence of unpaired electrons.

(ii) Chromium has higher melting and boiling points. In a particular series, the metallic strength increases upto middle with increasing number of unpaired electrons, *i.e.*, upto d^5 configuration. After Cr, the number of unpaired electrons goes on decreasing. Accordingly, the m.pt and b.pt. decrease after middle (Cr) because of increasing pairing of electrons.

23. $Mn^{3+}: 3d^4$

No. of unpaired electrons = 4

$Cr^{3+}: 3d^3$

No. of unpaired electrons = 3

Out of these, Cr^{3+} is most stable in aqueous solution due to half filled t_{2g} level, *i.e.*, t_{2g}^3.

24. $Ti^{3+}: 3d^1$

No of unpaired electrons = 1

$Cr^{3+}: 3d^3$

No. of unpaired electrons = 3

Out of these, Cr^{3+} is most stable in aqueous solution due to half filled t_{2g} level, *i.e.*, t_{2g}^3.

25. (i) Transition metals form alloys because they have similar atomic radii.

(ii) Basic nature of oxides decreases and acidic nature increases with increase in oxidation state of the metal. Oxidation state of Mn in Mn_2O_3 is +3 thus it is basic while in Mn_2O_7 it is +7 thus it is acidic.

26. (i) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

$E^\circ_{Cr^{3+}/Cr^{2+}}$ is negative (−0.41 V) whereas $E^\circ_{Fe^{3+}/Fe^{2+}}$ is positive (+0.77 V). Thus, Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+}. Hence, Cr^{2+} is stronger reducing agent than Fe^{2+}.

(ii) More positive is the value of E°, more feasible will be the reaction.

As $E^\circ_{Co^{3+}/Co^{2+}}$ is maximum, thus Co^{2+} ion is most stable.

27. (a) Cr^{2+} is reducing as its configuration changes from d^4 to d^3 and d^3 has stable half filled t_{2g}^3 configuration.

On the other hand change of Mn^{3+} to Mn^{2+} result in half-filled d^5 stable configuration thus Mn^{3+} acts as strong oxidizing agent.

(b) Transition metal ions with d^1 configuration have a tendency to lose this single electron and give ion with a noble gas configuration.

28. (i) Variable oxidation states of transition metals arise due to incomplete filling of *d*-orbitals and it differs from each other by unity *e.g.*, V(V), V(IV), V(III), V(II). In *p*-block elements oxidation states differ generally by a unit of two. *e.g.*, Sn(II), Sn(IV), PCl_3, PCl_5, etc.

(ii) In aqueous solution, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2Cu^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$

Hydration enthalpy of Cu^{2+} is higher than Cu^+ thus Cu^{2+} is more stable in aqueous solution.

29. (i) Transition elements can use their *ns* and $(n-1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

For example, Cr has $ns^2(n-1)\,d^4$ electronic configuration. It utilizes two electrons from its *ns* subshell then its oxidation state = +2. When it utilizes both the electrons, then its oxidation state = +3, +4 or +6.

(ii) In Zn, Cd and Hg, all the electrons in *d*-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.

30. (i) Manganese can form $p\pi$ - $d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$ - $d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(ii) Transition elements can use their *ns* and $(n-1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

31. (i) Transition elements can use their *ns* and $(n-1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

(ii) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$

Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

32. Transition elements can use their *ns* and (*n* – 1) *d*-orbital electrons for bond formation therefore, they show variable oxidation states.
Among the 3*d* series, manganese (Mn) exhibits the largest number of oxidation states from +2 to +7 because it has maximum number of unpaired electrons.
Mn – [Ar] $3d^5\ 4s^2$

33. (i) Manganese can form $p\pi$ - $d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$ - $d\pi$ bond thus, it can show a maximum of +4 oxidation state.
(ii) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples.

34. Disproportionation reaction involves the oxidation and reduction of the same substance. The example of disproportionation reaction in aqueous solution is :

$$2Cu^{+}_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$$

35. (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.
(ii) Zinc ($Z = 30$) has completely filled *d*-orbital ($3d^{10}$), so *d*-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

36. (i) Characteristics of transition elements :
(a) They show variable oxidation states.
(b) They exhibit catalytic properties.
(ii) Zn is considered as *d*-block element but not as transition element because it does not have partly filled *d*-orbitals in its atomic state or common oxidation states (*i.e.*, Zn^{2+}).

37. (i) The atoms of transition metals have strong metallic bonds between them due to the involvement of both (*n* – 1)*d* and *ns* electrons in bonding , thus these have high melting and boiling points.
(ii) Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d*-configurations (*e.g.*, d^0, d^5, d^{10} are exceptionally stable).

38. (i) In aqueous solution, Cu^{+} undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2Cu^{+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$

Hydration enthalpy of Cu^{2+} is higher than Cu^{+} that is why Cu^{2+} is more stable in aqueous solution.
(ii) This is due to ability of oxygen to form multiple bonds with metals.

39. (i) Transition elements can use their *ns* and (*n* – 1) *d*-orbital electrons for bond formation therefore, they show variable oxidation states. Because, the energy difference between (*n* –1)d orbital and *ns* orbital is small.
(ii) The tendency to form complexes is high for Co(III) as compared to Co(II). Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, *e.g.*,

$$[Co(NH_3)_6]^{2+} \xrightarrow{Air} [Co(NH_3)_6]^{3+}$$

This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a d^7 $(t_{2g}^6\ e_g^1)$ arrangement.

40. (i) In aqueous solution Cu^{+} undergoes disproportionation to form a more stable Cu^{2+} ion.

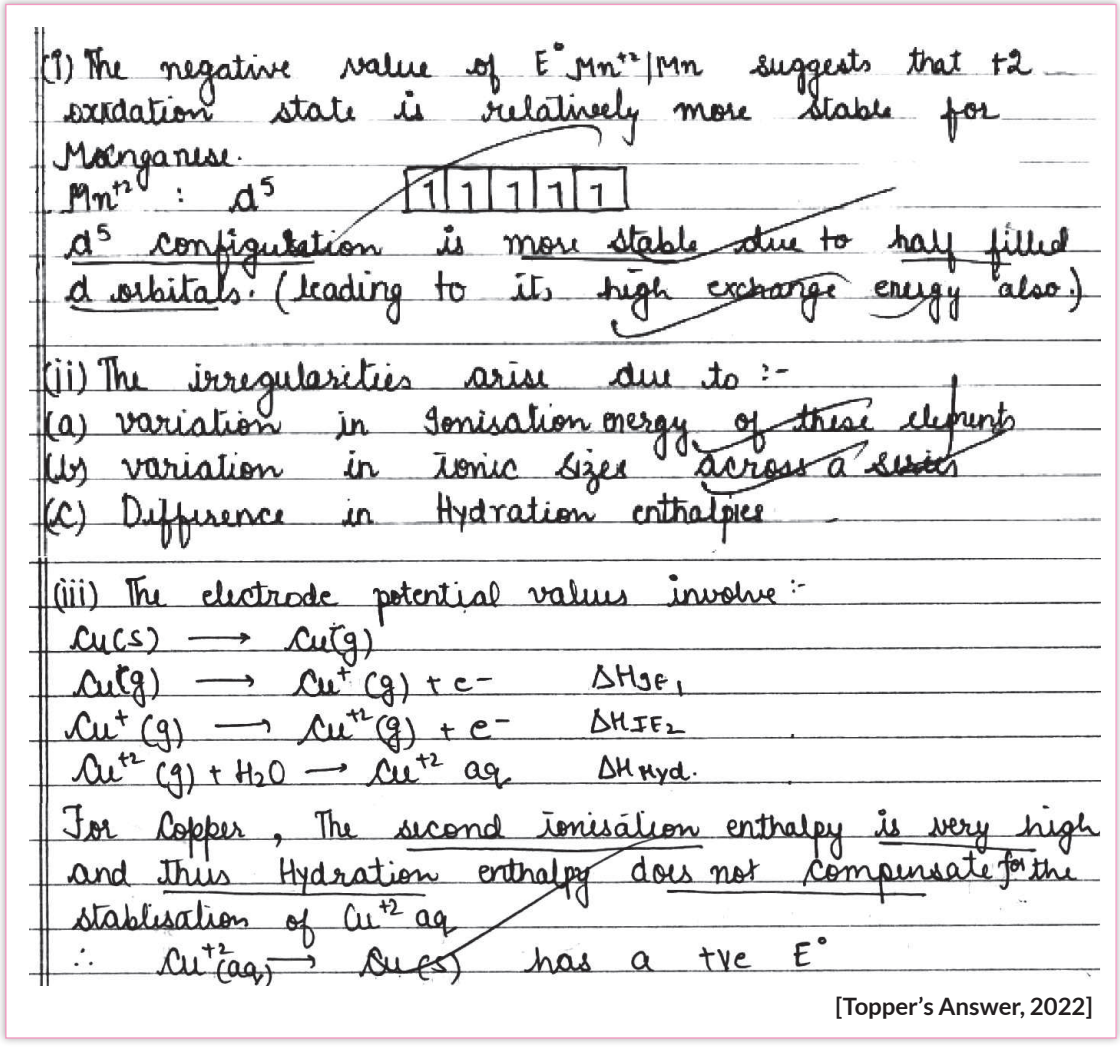
$$2Cu^{+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$

Hydration enthalpy of Cu^{2+} is higher than Cu^{+} that is why Cu^{2+} is more stable in aqueous solution.
(ii) Transition elements have more number of unpaired electron in their valence shells than alkali metals, that is why transition elements make strong metallic bonds, which results in extreme hardness as compared to alkali metals.

41. (i) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. For example, vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation).
(ii) Due to presence of vacant *d*-orbitals, there is *d*-*d* transitions in the compounds of the transition metals that is why they are generally coloured.
When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

42. (i) Cr^{3+} is most stable, because of stable t_{2g}^3 electronic configuration of Cr^{3+} in aqueous solution.
(ii) Mn^{3+} is the strongest oxidising agent. Mn^{3+} on reduction gives Mn^{2+} which is quite stable due to half filled $3d^5$ electronic configuration.
(iii) Due to absence of unpaired electron in Ti^{4+}, it is a colourless ion.
E.C. of Ti^{4+} = $[Ar]3d^0 4s^0$

43.


(i) The negative value of $E^\circ_{Mn^{+2}|Mn}$ suggests that +2 oxidation state is relatively more stable for Manganese.

Mn^{+2} : d^5 | 1 | 1 | 1 | 1 | 1 |

d^5 configuration is more stable due to half filled d orbitals. (leading to its high exchange energy also.)

(ii) The irregularities arise due to :-
(a) variation in Ionisation energy of these elements
(b) variation in ionic sizes across a series
(c) Difference in Hydration enthalpies

(iii) The electrode potential values involve :-

$Cu(s) \longrightarrow Cu(g)$

$Cu(g) \longrightarrow Cu^+(g) + e^-$ $\quad \Delta H_{IF_1}$

$Cu^+(g) \longrightarrow Cu^{+2}(g) + e^-$ $\quad \Delta H_{IF_2}$

$Cu^{+2}(g) + H_2O \longrightarrow Cu^{+2}\,aq$ $\quad \Delta H_{Hyd.}$

For Copper, The second ionisation enthalpy is very high and Thus Hydration enthalpy does not compensate for the stablisation of Cu^{+2} aq

$\therefore$ $Cu^{+2}(aq) \longrightarrow Cu(s)$ has a +ve E°

[Topper's Answer, 2022]

44. (i) Zn^{2+} ion has completely filled *d*-subshell and no *d-d* transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is [Ar] $3d^9$. It has partly filled *d*-subshell and hence it is coloured due to *d-d* transition.

(ii) E° value of Mn^{3+}/Mn^{2+} is + 1.57 V.

$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)}$; E° = +1.57 V

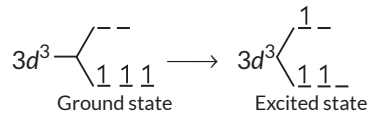
This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

(iii) Transition metals form alloys because they have similar atomic radii.

45. (i) Colour of transition metal ions is due to the *d-d* transitions. Ions which do not involve in *d-d* transitions are colourless.

Ti^{4+} : $3d^0 4s^0$, No unpaired *d*-electrons, so no *d-d* transition, colourless

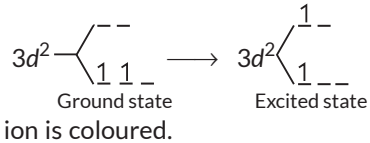
Cr^{3+} : $3d^3$, *d-d* transitions occur as shown below :



Ground state $\qquad$ Excited state

Hence, Cr^{3+} ion is coloured.

V^{3+} : d^2, *d-d* transition occur as shown below :



Ground state $\qquad$ Excited state

Hence, V^{3+} ion is coloured.

In other words, Generally the ions having completely empty *d*-orbitals or no unpaired electron in *d*-orbitals of transition element are colourless.

(ii) $Mn^{2+}(3d^5) \longrightarrow Mn^{3+}(3d^4)$

More stable $\qquad$ Less stable

Mn^{2+} is more stable in $3d^5$ state, hence shows resistance towards oxidation.

$Fe^{2+}(3d^6) \longrightarrow Fe^{3+}(3d^5)$

Less stable $\qquad$ More stable

Fe^{3+} is more stable hence Fe^{2+} gets oxidised easily to Fe^{3+}.

(iii) Highest oxidation state of transition element is shown with oxides and fluorides, because oxygen and flourine are small in size and have high electronegativity.

46. (i) Silver atom has outer electronic configuration $4d^{10}\,5s^1$ in its ground state, but silver in +2 oxidation state has electronic configuration $4d^9$. So in +2 oxidation state, silver has incomplete *d*-orbital. Hence, silver is considered as a transition element.
(ii) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration whereas Zn^{2+} has completely filled d^{10} configuration. Hence, $E°_{Mn^{2+}/Mn}$ and $E°_{Zn^{2+}/Zn}$ are more negative than expected.

(iii) Transition metals form alloys because they have similar atomic radii.

47. (a) In case of copper, the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. That is why $E°_{M^{2+}/M}$ for Cu is positive. So, copper does not displace hydrogen from acids.
(b) Transition metals and most of their compounds contain unpaired electrons in the $(n-1)d$-orbitals. Hence, they show paramagnetic behaviour.
(c) In Zn, Cd and Hg, all the electrons in *d*-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.

48. (i) The high melting points of transition metals are attributed to the involvement of greater number of $(n-1)d$ electrons in addition to *ns* electrons in the interatomic metallic bonding. In any row, the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases.
(ii) Due to presence of vacant *d*-orbitals and *d-d* transitions, compounds of the transition metals are generally coloured.
When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

(iii) $E°$ value of Mn^{3+}/Mn^{2+} is + 1.57 V.

$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)} \; ; \; E° = +1.57 \text{ V}$$

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

49. (i) Enthalpy of atomisation depends on the number of unpaired electrons in the valence shell. Greater the number of valence electrons, stronger is the resultant bonding and higher will be the enthalpy of atomisation. In 3*d* series, zinc has no unpaired electrons in valence shell so, it has lowest enthalpy of atomisation.
(ii) The enthalpies of second and third transition series are high because of the poor shielding of electrons in 4*d* and 5*d* orbitals in comparison to electrons in 3*d* orbital which results in strong metallic bonding.
(iii) Transition metals have high enthalpies of atomisation because of presence of unpaired electrons and poor shielding effect of *d*-orbitals.

50. Elements which have incompletely filled *d*-orbitals in their ground state or in any one of their oxidation states are called transition elements.
Zn, Cd, Hg are considered as *d*-block elements but not as transition elements because they do not have partly filled *d*-orbitals in their atomic state or their common oxidation states (*i.e.*, Zn^{2+}, Cd^{2+}, Hg^{2+}).
Variable oxidation states of transition metals arise due to incomplete filling of *d*-orbitals and it differs from each other by unity *e.g.*, V(V), V(IV), V(III), V(II). In *p*-block elements oxidation states differ generally by a unit of two. *e.g.*, Sn(II), Sn(IV), PCl_3, PCl_5, etc.

51. (a) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.
(b) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence $E°_{Mn^{2+}/Mn}$ is more negative.
(c) Cr^{2+} is a strong reducing agent since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

52. (a) Transition elements can use their *ns* and $(n-1)$ *d*-orbital electrons for bond formation therefore, they show variable oxidation states. Because, the energy difference between $(n-1)d$ orbital and *ns* orbital is small.
(b) Electrode potential ($E°$) value is the sum of three factors :
(i) Enthalpy of sublimation, $\Delta_{sub}H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$
(ii) Ionisation enthalpy, Δ_iH for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$
(iii) Hydration enthalpy, $\Delta_{hyd}H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of sublimation and ionisation enthalpy is greater than enthalpy of hydration. This is why $E°_{M^{2+}/M}$ for Cu is positive.

(c) Cr^{2+} is reducing since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.

53. Elements which have incompletely filled *d*-orbitals in their ground state or in any one of their oxidation states are called transition elements
The following are the characteristics of transition elements :
(a) They show variable oxidation states.
(b) They exhibit catalytic properties.

54. (a) Electrode potential ($E°$) value is the sum of three factors :

(i) Enthalpy of sublimation $\Delta_{sub}H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$
(ii) Ionisation enthalpy Δ_iH for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$
(iii) Hydration enthalpy $\Delta_{hyd}H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of sublimation and ionisation enthalpy is greater than enthalpy of hydration. This is why $E^{\circ}_{M^{2+}/M}$ for Cu is positive.

(b) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

55. (i) Transition metal form alloys because they have similar atomic radii.
(ii) Due to fully filled *d*-orbital (d^{10}), Zn has weak metallic bond, thus it has lowest enthalpy of atomization.
(iii) Manganese can from $p\pi$-$d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$-$d\pi$ bond thus, it can show a maximum of +4 oxidation state.

56. (i) Cr^{2+} is a strong reducing agent since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.
(ii) Cu^+ is unstable in aqueous solution
In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

(iii) Mn^{3+} is a strong oxidising agent because electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily.

Key Points

- Species tends to act as oxidising and reducing agent to attain most stable oxidation state.

57. (i) From the relation, $\Delta G^{\circ} = -nFE^{\circ}$
More positive is the value of E°, reaction will be feasible.

$$\underset{3d^4}{Mn^{3+}} \xrightarrow{+e^-} \underset{\substack{3d^5\\ \text{More stable}\\ \text{(half filled)}}}{Mn^{2+}} \quad ; \quad \underset{3d^5}{Fe^{3+}} \xrightarrow{+e^-} \underset{\substack{3d^6\\ \text{More stable}\\ \text{(half filled)}}}{Fe^{2+}}$$

Hence, E°_{value} for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(ii) Greater the number of unpaired electrons, stronger is the metallic bond and therefore, higher is the enthalpy of atomisation. Since, iron has greater number of unpaired electrons than copper hence has higher enthalpy of atomisation.

(iii) Only those ions are coloured which have partially filled *d*-orbitals facilitating *d*-*d* transitions. Sc^{3+} has no unpaired electron but Ti^{3+} has one unpaired electron and hence, Ti^{3+} is coloured.

58. (i) Transition metals form a large number of complex compounds due to following reasons :
- Comparatively smaller size of metal ions.
- High ionic charges.
- Availability of *d*-orbitals for bond formation.

(ii) Lowest oxidation compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas, the higher oxidation state of metal and compounds gets reduced to lower ones and hence are acidic in nature.

e.g., MnO is basic whereas Mn_2O_7 is acidic.

(iii) E° value of Mn^{3+}/Mn^{2+} is + 1.57 V.

$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)}$; $E^{\circ} = +1.57$ V

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

59. (i) Manganese can form $p\pi$ - $d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$ - $d\pi$ bond thus, it can show a maximum of +4 oxidation state.
(ii) Cr^{2+} is a strong reducing agent since its configuration is converted to d^3 from d^4. d^3 has half filled t_{2g} configuration with higher stability.
(iii) Zn^{2+} ion has completely filled *d*-subshell and no *d*-*d* transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is [Ar] $3d^9$. It has partly filled *d*-subshell and hence it is coloured due to *d*-*d* transition.

60. (i) In case of copper, the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. That is why $E^{\circ}_{M^{2+}/M}$ for Cu is positive.
(ii) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence $E^{\circ}_{Mn^{2+}/Mn}$ is more negative.
(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

$E^{\circ}_{Cr^{3+}/Cr^{2+}}$ is negative (– 0.41 V) whereas $E^{\circ}_{Fe^{3+}/Fe^{2+}}$ is positive (+ 0.77 V). Thus Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+}. Hence, Cr^{2+} is stronger reducing agent than Fe^{2+}.

Concept Applied

- $Cu^{2+}_{(aq)}$ is more stable than $Cu^+_{(aq)}$ due to the more negative value of $\Delta_{Hyd}H^{\circ}$ of Cu^{2+} than Cu^+.

61. (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.
(ii) Zinc ($Z = 30$) has completely filled *d*-orbital ($3d^{10}$), so *d*-orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

(iii) Only those ions are coloured which have partially filled *d*-orbitals facilitating *d-d* transitions.

Sc^{3+} with $3d^0$ configuration is colourless while Ti^{3+} ($3d^1$) is coloured.

62. (i) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7, Example - MnO_3F.

(ii) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

(iii) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the later having a half-filled t_{2g} level, on the other hand, the change from Mn^{3+} to Mn^{2+} result in the half-filled (d^5) configuration which has extra stability.

(iv) Zn does not have unpaired electrons due to which metal-metal bonding is weak so Zn has lowest enthalpy of atomisation.

(v) Copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

The stability of $Cu^{2+}(aq)$ rather than $Cu^+(aq)$ is due to the much more negative $\Delta_{hyd}H°$ of $Cu^{2+}(aq)$ than $Cu^+(aq)$, which more than compensates for second ionisation enthalpy of Cu.

63. (i) Mn shows maximum no. of oxidation states from +2 to +7 because Mn has maximum number of unpaired electrons in 3*d* sub-shell.

(ii) Cr has maximum melting point, because it has 6 unpaired electrons in the valence shell, hence it has strong interatomic interaction.

(iii) Sc shows only +3 oxidation state because after losing 3 electrons, it has noble gas electronic configuration.

(iv) Mn is strong oxidising agent in +3 oxidation state because change of Mn^{3+} to Mn^{2+} give stable half filled (d^5) electronic configuration,

$E°_{(Mn^{3+}/Mn^{2+})} = 1.5$ V.

64. In aqueous solution,

$$\underset{\text{Dichromate ion (Orange red)}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\text{Chromate ion (Yellow)}}{2CrO_4^{2-}} + 2H^+$$

When an acid is added (*i.e.*, pH of solution decreased), the concentration of H^+ ions is increased and the reaction proceeds in the backward direction producing an orange red dichromate solution.

65. $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

66. $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

67. Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali such as NaOH is added because on addition of an alkali, the concentration of H^+ ions decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

68. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

69. $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

70. (a) $\Delta G° = -nFE°$

More positive is the $E°$ value, reaction will be more feasible.

$$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)} ; E° = +1.57 \text{ V}$$

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

$$\underset{3d^5}{Fe^{3+}} + e^- \longrightarrow \underset{3d^6}{Fe^{2+}} ; E° = +0.77 \text{ V}$$

(More stable)

$$Cr^{3+} + e^- \longrightarrow Cr^{2+} ; E° = -0.41 \text{ V}$$

(b) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

71. (a) $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

(b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

72. Preparation of potassium permanganate : Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

or, $3K_2MnO_4 + 4HCl \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

73. (i) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$.

74. (i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

(ii) Sodium dichromate can be crystallised out from sodium chromate solution by acidifying it with sulphuric acid.

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

75. (i) Yellow solution of Na_2CrO_4 is filtered and acidified with conc. H_2SO_4 acid to give $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(ii) Sodium dichromate solution is treated with KCl to give $K_2Cr_2O_7$.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

This reaction occurs because potassium dichromate is less soluble than sodium dichromate.

76. (*A*) is K_2MnO_4, (*B*) is $KMnO_4$, (*C*) is KIO_3 and (*D*) is I_2.

$$MnO_2 + 2KOH + KNO_3 \longrightarrow \underset{(A)}{K_2MnO_4} + KNO_2 + H_2O$$

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow \underset{(B)}{2KMnO_4} + MnO_2 + 2K_2SO_4 + 2H_2O$$

$$2KMnO_4 + H_2O + KI \longrightarrow 2MnO_2 + 2KOH + \underset{(C)}{KIO_3}$$

$2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$ (*D*)

77. (i) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(ii) $2MnO_4^- + H_2O + I^- \rightarrow 2OH^- + 2MnO_2 + IO_3^-$

78. (i) $2MnO^-{}_4 + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(ii) $2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$

79. (i) $4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$ (*A*)

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ (*B*)

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$ (*C*)

(ii) Potassium dichromate is used as a powerful oxidising agent in industries and for staining and tanning of leather.

Key Points

➲ Students must remember the equations involved in the preparation of potassium dichromate.

80. (i) $8MnO_{4\,(aq)}^- + 3S_2O_{3\,(aq)}^{2-} + H_2O_{(l)} \rightarrow 8MnO_{2(aq)} + 6SO_{4\,(aq)}^{2-} + 2OH^-_{(aq)}$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

81. (i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

82. Potassium dichromate is a strong oxidising agent. In the presence of dilute sulphuric acid, one molecule of $K_2Cr_2O_7$ gives 3 atoms of available oxygen.

(i) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(ii) $K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3S + K_2SO_4 + 7H_2O$

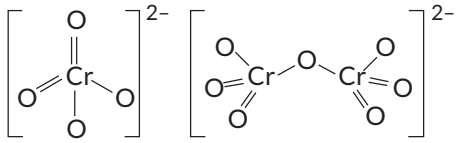
83. (i) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

84. (i) $5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$

(ii) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

85. On decreasing pH, *i.e.*, on acidifying, yellow colour of CrO_4^{2-} changes to $Cr_2O_7^{2-}$ (orange) while on increasing pH, *i.e.*, on treating with alkalies, orange colour of $Cr_2O_7^{2-}$ changes to CrO_4^{2-} (Yellow).



Chromate ion (Yellow) Dichromate ion (Orange)

86. The yellow solution of sodium chromate is acidified with sulphuric acid to give an orange solution of sodium dichromate $Na_2Cr_2O_7$ which is crystallised.

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Sodium chromate Sodium dichromate

The solution of sodium dichromate is treated with potassium chloride to obtain potassium dichromate.

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Potassium dichromate

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

87. $FeCr_2O_4 + Na_2CO_3 \longrightarrow 2Na_2CrO_4 + Fe_2O_3 + CO_2$ (*A*)

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ (*B*)

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$ (*C*)

$K_2Cr_2O + H_2SO_4 + Na_2SO_3 \longrightarrow K_2SO_4 + Na_2Cr_2O_7 + H_2O + SO_2$

88. (i) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

(ii) $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

(iii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

89. (a) (i) In 3*d* series, Mn has maximum number of oxidation state because number of unpaired electrons is maximum in Mn ($3d^5, 4s^2$).

(ii) $E°$ value of Mn^{3+}/Mn^{2+} is + 1.57 V.

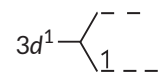
$Mn^{3+}_{(aq)} + e^- \longrightarrow Mn^{2+}_{(aq)}$; $E° = +1.57$ V

This value is highly positive because Mn^{3+} (d^4) has a very high tendency to get reduced to Mn^{2+} (d^5) which has a stable half - filled electronic configuration.

(iii) Colour of transition metal ions is due to the *d-d* transitions. Ions which do not involve in *d-d* transitions are colourless.

Ti^{4+} : $3d^0 4s^0$, no *d-d* transition, colourless

V^{4+} : d^1, *d-d* transition occur as shown below :



Hence, V^{4+} ion is coloured.

In other words, generally the ions having completely empty *d*-orbitals or no unpaired electron in *d*-orbitals of transition element are colourless.

(b) Preparation of potassium permanganate : Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

or, $3K_2MnO_4 + 4HCl \rightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(Purple colour) (Colourless)

90. (a) (i) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

(ii) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

(b) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali such as NaOH is added because on addition of an alkali, the concentration of H^+ ions

decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

91. (c) : As we move along the lanthanoid series, the nuclear charge increases by one unit at each successive element. The new electron is added into the same subshell *i.e.*, 4*f*. As a result, the attraction of the electrons by the nucleus increases and this tends to decrease the size. Further, as the new electron is added into the *f*-subshell, there is imperfect shielding of one electron by another in this subshell due to the shapes of these *f*-orbitals. This imperfect shielding is unable to counter balance the effect of increased nuclear charge.

92. (b): The most stable and common oxidation state of a lanthanoid is +3. However, some elements show variable oxidation state they try to lose or gain electrons to get +3 states, which makes them strong reducing or oxidising agents respectively.

93. (a): All lanthanoids show +3 as the common oxidation state, yet Ce shows +4 oxidation state due to attainment of noble gas configuration.
Ce^{4+}: [Xe]$4f^0$

94. Eu^{2+} has a strong tendency to lose electrons to attain the more stable +3 oxidation state of lanthanoids hence, it is a strong reducing agent.

95. Due to lanthanoid contraction the elements of 4*d* and 5*d*-series have similar atomic radii *e.g.*, Zr = 145 pm and Hf = 144 pm.

96. Europium (Eu) is well known to exhibit +2 oxidation state due to its half-filled *f* orbital in +2 oxidation state.

97. Lanthanoids showing +4 oxidation state are $_{58}Ce$, $_{59}Pr$, $_{65}Tb$ and $_{66}Dy$.

98. Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.

e.g., $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$
$Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

99. (a) **Lanthanoid contraction :** The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

Consequences of lanthanoid contraction :

(i) Atomic radii of second and third transition series element are almost identical. As a result they occur in nature together and their separation from mixutre different.

(ii) The small difference in atomic radii of lanthanoids is responsible for difference in their basic properties.

(b) Among the 3*d* series, Mn exhibits largest number of oxidation states from +2 to +7 because it has maximum number of unpaired electrons.

100. (i) Because of large number of unpaired electrons in their atoms they have stronger interatomic attraction and hence stronger metallic bonding between atoms resulting in higher enthalpies of atomisation.

(ii) Separation of a mixture of lanthanoids is difficult because they have similar atomic radius due to lanthanoid contraction and similar chemical properties.

(iii) Electrode potential ($E°$) value is the sum of three factors :

1. Enthalpy of sublimation $\Delta_{sub}H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$
2. Ionisation enthalpy Δ_iH for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$
3. Hydration enthalpy $\Delta_{hyd}H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of sublimation and ionisation enthalpy is greater than enthalpy of hydration. This is why $E^\circ_{M^{2+}/M}$ for Cu is positive.

101. (i) +3 is the most common oxidation state in lanthanoids.

(ii) From left to right in a transition series, atomic number increases. Number of protons in the nucleus and number of electrons in the penultimate shell increases. *d*-electrons have very poor shielding power. Thus, effective nuclear charge increases. Nuclear attractive force on the outermost electron increases and hence atomic and ionic radii decreases.

(iii) V(23) : [Ar]$3d^3\ 4s^2$
V^{3+}: [Ar] $3d^2$
No. of unpaired e^- = 2
Ti(22) : [Ar]$3d^2\ 4s^2$
Ti^{3+} : [Ar] $3d^1$
No. of unpaired e^- = 1

102. (i) Ce(58) : [Xe]$4f^15d^16s^2$
Ce^{3+} : [Xe]$4f^1$

$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3}$ = 1.73 B.M.

(ii) Copper atom has completely filled *d*-orbital ($3d^{10}$) in its ground state.
But in its most common oxidation state of +2 , the configuration is d^9, *i.e.*, the *d*-subshell is incompletely filled. Hence, it is a transition element.

(iii) Only those ions are coloured which have partially filled *d*-orbitals facilitating *d-d* transitions. Sc^{3+} has no unpaired electron but Ti^{3+} has one unpaired electron and hence, Ti^{3+} is coloured.

103. Lanthanoid contraction : The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

Consequences of lanthanoid contraction :

(i) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(ii) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar. *e.g.*, atomic radii of zirconium(Zr) is same as that of hafnium Hf.

104. (a) (i) At. no. of Cr is 24.
Electronic configuration : [Ar] $3d^54s^1$
Cr^{3+} : [Ar]$3d^3$

No. of unpaired $e^- = 3$

(ii) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

(b) (i) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(ii) In case of copper, the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. That is why $E^\ominus_{M^{2+}/M}$ for Cu is positive.

(iii) Eu^{2+} has a strong tendency to lose electrons to attain the more stable +3 oxidation state of lanthanoids hence, it is a strong reducing agent.

105. (a) (i) Transition metal and their compounds show catalytic activities due to their ability to adopt multiple oxidation states, ability to absorb the reactant(s) and ability to form complexes.

(ii) Separation of a mixture of lanthanoids is difficult because they have similar atomic radius due to lanthanoid contraction and similar chemical properties.

(iii) In Zn, Cd and Hg, all the electrons in *d*-subshell are paired. Hence, the metallic bonds are weak. That is why they are soft metals with low melting and boiling points.

(b) (i) The yellow solution of sodium chromate is acidified with sulphuric acid to give a orange solution of sodium dichromate $Na_2Cr_2O_7$, which is crystallized.

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

(ii) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$

106. The irregularities in the electronic configurations of actinoids are due to extra stabilities of the f^0, f^7 and f^{14} orbitals.

107. The actinoid contraction is more than lanthanoid contraction because 5*f*-electrons are more poorly shielded than 4*f*-electrons.

108. Similarity : The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.

Difference : Lanthanoids except promethium are non-radioactive elements, while all actinoids are radioactive elements.

109. Chemistry of actinoids is more complicated than lanthanoids because

(i) actinoids show greater number of oxidation states due to the comparable energies of 5*f*, 6*d* and 7*s* orbitals.

(ii) most of the actinoids are radioactive and the study of their chemistry in the laboratory is difficult.

110. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids.

111. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids. Similarity : The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.

112. **Structure :** All the lanthanoids are silvery white soft metals. Hardness of Lanthanoids increases with increasing atomic number.

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is due to irregularities in metallic radii which are greater than that of lanthanoids.

Chemical reactivity : Earlier members of lanthanoid series are quite reactive similar to calcium but with increasing atomic number they behave more like aluminium.

The actinoids are highly reactive in finely divided state.

113. Difference between lanthanoids and actinoids are following :

(i) Electronic configuration : The general electronic configuration of lanthanoids is $[Xe]4f^{1-14}\ 5d^{0-1}\ 6s^2$ whereas, that of actinoids is $[Rn]\ 5f^{\ 1-14}\ 6d^{0-1}\ 7s^2$. Thus, lanthanoids involve the filling of 4*f*-orbitals whereas, actinoids involve the filling of 5*f*-orbitals.

(ii) Oxidation states : Lanthanoids have principal oxidation state of +3. In addition, the lanthanoids show limited oxidation states such as +2 and +4 because of small energy gap between 4*f* and 5*d* subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between 5*f* and 6*d* subshells.

(iii) Chemical reactivity : First few members of lanthanoids are quite reactive almost like calcium, whereas, actinoids are highly reactive metals especially in the finely divided state. Lanthanoids react with dilute acids to liberate H_2 gas whereas actinoids react with boiling water to give a mixture of oxide and hydride.

Key Points

- In actinoids, neptunium (Np) and plutonium (Pu) show maximum oxidation states upto +3 to +7.

114. (a) : General electronic configuration of lanthanoids is $4f^{1-14}5d^{0-1}6s^2$.

(b) Cerium shows +3, +4 oxidation states.

(c) Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals in actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids.

CBSE Sample Questions

1. (b) **(1)**

2. (c) : V^{3+}, V^{2+}, Fe^{3+} possesses two, three and five unpaired electrons in 3*d*-subshell. Hence, they will give coloured solution. **(1)**

3. **(b):** V^{2+} : $3d^3$ ⇒ No. of unpaired electrons = 3
⇒ paramagnetic
Sc^{3+} : $3d^0$ ⇒ No. of unpaired electrons is zero
⇒ diamagnetic
Cu^{2+} : $3d^9$ ⇒ No. of unpaired electron = 1
⇒ paramagnetic
Mn^{3+} : $3d^4$ ⇒ No. of unpaired electrons = 4 **(1)**
⇒ paramagnetic

4. (a) The ability of fluorine to stabilise the highest oxidation state is attributed to the higher lattice energy or high bond enthalpy. **(1)**

(b) Co^{2+} has three unpaired electrons so it would be paramagnetic in nature, hence Co^{2+} ion would be attracted to magnetic field. Rest all ions are diamagnetic in nature. **(1)**

(c) The transition elements of 5*d* series have intervening 4*f* orbitals. There is greater effective nuclear charge acting on outer valence electrons due to the weak shielding by 4*f* electrons. Hence, first ionisation energy of 5*d* series of transition elements are higher than that of 3*d* and 4*d* series. **(1)**

OR

(a) Manganese has five unpaired electrons in its *d*-orbital which is completely half filled and having more stability. Hence, these electrons are not free to participate in metallic bonding. So, Mn has less heat of atomization and its melting point is lower than chromium. **(1)**

(b) The 4*d* and 5*d* transition elements have larger size than that of 3*d* elements. They form strong metal-metal bond which required more energy to break bond. That is why 3*d* series have lower melting point than 4*d* series. **(1)**

(c) Tungsten (W). **(1)**

5. (a) Ti is having electronic configuration [Ar]$3d^2\ 4s^2$ which on loss of four electrons will lead to the formation of Ti^{4+} [Ti(IV)] which is more stable as it acquires nearest noble gas configuration. **(1)**

(b) In case of transition elements, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. As the new electron enters in *d*-orbital each time the nuclear charge increases by unity. The shielding effect of a *d* electrons is not that effective, hence the net electrostatic attraction between the nucleus and the outermost electron increases and the ionic radius decreases. **(1)**

(c) Iron and chromium are having high enthalpy of atomization due to the presence of unpaired electrons, which accounts for their hardness. However, zinc has low enthalpy of atomization as it has no unpaired electron. Hence, zinc is comparatively a soft metal. **(1)**

6. (i) The transition elements are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to absorb the reactant(s) and ability to form complexes. **(1)**

(ii) Due to high value of third ionisation enthalpy. **(1)**

(iii) Mo(VI) and W(VI) are more stable than Cr(VI). **(1)**

OR

(i) The general trend towards less negative $E°$ values across the series is related to the general increase in the sum of first and second ionization enthalpies. **(1)**

(ii) Copper has high positive reduction potential ($E°$ value) and this show that copper is least reactive metal. Electrode potential ($E°$) value is the sum of three factors.

(a) Enthalpy of atomisation, $\Delta_a H$ for $Cu_{(s)} \rightarrow Cu_{(g)}$.

(b) Ionisation enthalpy, $\Delta_i H$ for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$

(c) Hydration enthalpy, $\Delta_{hyd} H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is is not balanced enthalpy of hydration. This is why $E°_{M^{2+}/M}$ for Cu is positive. **(1)**

(iii) Mn^{2+} ion and Zn^{2+} ion has stable half-filled($3d^5$) and fully-filled ($3d^{10}$) electronic configuration. Hence $E°_{Mn^{2+}/Mn}$ and $E°_{Zn^{2+}/Zn}$ is more negative. **(1)**

7. **(b):** Charge transfer from ligand to metal.
The Mn atom in $KMnO_4$ has +7 oxidation state with electronic configuration [Ar]$3d^0 4s^0$. Since no unpaired electrons are present, *d-d* transitions are not possible. The molecule should, therefore, be colourless. But its intense purple colour is due to $L \rightarrow M$ (ligand to metal) charge transfer 2*p*(*L*) of O to 3*d*(*M*) of Mn. **(1)**

8. (a) Cu^{2+} oxidizes iodide ion to iodine. **(1)**

(b) The low value for V is due to the stability of V^{2+} having half-filled t_{2g} level. **(1)**

(c) Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine. **(1)**

(d) The *d* orbital is full with ten electrons and shield the electrons present in the higher *s*-orbital to a greater extent resulting in increase in size. **(1)**

(e) The chromates and dichromates are inter-convertible in aqueous solution depending upon pH of the solution. Increasing the pH (in basic solution) of dichromate ions a colour change from orange to yellow is observed as dichromate ions change to chromate ions. **(1)**

9. **(b):** The magnetic moment is less as the 5*f* electrons of actinides are less effectively shielded which results in quenching of orbital contributions. They are strongly paramagnetic due to presence of unpaired electrons. **(1)**

Self Assessment

Case Based Questions (5 marks)

1. Read the passage given below and answer the following questions :

Transition metal oxides are compounds formed by the reaction of metals with oxygen at high temperature. The highest oxidation number in the oxides coincides with the group number. In vanadium, there is a gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5·V_2O_4 dissolves in acids to give VO^{2+} salts. Transition metal oxides are commonly utilized for their catalytic activity and semiconductive properties. Transition metal oxides are also frequently used as pigments in paints and plastic. Most notably titanium dioxide. One of the earliest application of transition metal oxides to chemical industry involved the use of vanadium oxide for catalytic oxidation of sulphur dioxide to sulphuric acid. Since then, many other applications have emerged, which include benzene oxidation to maleic anhydride on vandium oxides; cyclohexane oxidation to adipic acid on cobalt oxides. An important property of the catalyst material used in these processes is the ability of transition metals to change their oxidation state under a given chemical potential of reductants and oxidants.

(i) Which oxide of vanadium is most likely to be basic and ionic ?

(a) VO (b) V_2O_3
(c) VO_2 (d) V_2O_5

(ii) Vanadyl ion is

(a) VO^{2+} (b) VO_2^+
(c) V_2O^+ (d) VO_4^{3-}

(iii) Which of the following statements is false?

(a) With fluorine vanadium can form VF_5.
(b) With chlorine vanadium can form VCl_5.
(c) Vanadium exhibits highest oxidation state in oxohalides $VOCl_3$, $VOBr_3$ and fluoride VF_5.
(d) With iodine vanadium cannot form VI_5 due to oxidising power of V^{5+} and reducing nature of I^-.

(iv) The oxidation state of vanadium in V_2O_5 is

(a) +5/2 (b) +7 (c) +5 (d) +6

(v) Identify the oxidising agent in the following reaction.

$$V_2O_5 + 5Ca \longrightarrow 2V + 5CaO$$

(a) V_2O_5 (b) Ca
(c) V (d) None of these

A & R Questions (1 mark)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

2. Assertion : Separation of Zr and Hf is difficult.
Reason : Zr and Hf lie in the same group of the periodic table.

3. Assertion : Actinoids form relatively less stable complexes as compared to lanthanoids.
Reason : Actinoids can utilise their 5*f* orbitals along with 6*d* orbitals in bonding but lanthanoids do not use their 4*f* orbital for bonding.

Multiple Choice Questions (1 mark)

4. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?

(a) They have high melting points in comparison to pure metals.
(b) They are very hard.
(c) They retain metallic conductivity.
(d) They are chemically very reactive.

5. When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salts then Sn^{2+} changes to

(a) Sn (b) Sn^{3+} (c) Sn^{4+} (d) Sn^+

OR

Electronic configuration of a transition element *X* in +3 oxidation state is [Ar]$3d^5$. What is its atomic number?

(a) 25 (b) 26 (c) 27 (d) 24

6. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is

(a) 2.87 B.M. (b) 3.87 B.M.
(c) 3.47 B.M. (d) 3.57 B.M.

7. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?

(a) U (b) Np (c) Tm (d) Fm

8. Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?
(a) Ag_2SO_4 (b) CuF_2
(c) ZnF_2 (d) Cu_2Cl_2

VSA Type Questions (1 mark)

9. CuI_2 is not known. Why ?

10. What are coinage metals? Why are they so called?

11. Second ionisation enthalpy for Cr and Cu is unusually high. Explain.

SA I Type Questions (2 marks)

12. Trivalent lanthanoid ions are coloured. Why?

13. Discuss the consequences of lanthanoid contraction.

14. Ionisation enthalpies of actinoids are lower than that of corresponding lanthanoids. Why?

15. How is potassium permanganate prepared in laboratory?

16. What happens when $KMnO_4$ is heated?

OR

Electronic configuration of actinoids are irregular. Why?

SA II Type Questions (3 marks)

17. (i) Complete the following reactions :
(a) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow$
(b) $5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow$
(ii) Give two uses of $KMnO_4$.

18. Give reasons :
Anhydrous cobalt compounds appear blue while hydrated compounds appear red.

19. Transition metals have very high melting and boiling points. Why?

20. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation.

OR

(i) Give two reactions in which potassium dichromate acts as oxidising agent.
(ii) What happens when dichromate ion is dissolved in alkali?

Case Based Questions (4 marks)

21. Read the passage given below and answer the following questions :

Transition elements are elements that have partially filled *d*-orbitals. The configuration of these elements corresponds to $(n-1)d^{1\text{-}10}\ ns^{1\text{-}2}$. It is important to note that the elements mercury, cadmium and zinc are not considered transition elements because of their electronic configurations, which corresponds to $(n-1)d^{10}ns^2$. Some general properties of transition elements are :
These elements exhibit many oxidation states ;
These elements can form coloured compounds and ions due to *d-d* transition;
These elements exhibit many oxidation states ;
These elements exhibit paramagnetic or diamagnetic properties which depends on no. of unpaired electron in atom or ion.
A large variety of ligands can bind themselves to these elements, due to this, a wide variety of stable complexes formed by these ions. The boiling and melting point of these elements are high. These elements have a large ratio of charge to the radius.
General electronic configuration :
$(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$

(i) The magnetic nature of elements depends on the presence of unpaired electrons. Identify out of $3d^7$, $3d^8$, $3d^5$ and $3d^2$ configuration of transition element, which shows highest magnetic moment.

(ii) Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Mn	Fe	Co	Cu
Metallic radii/pm	137	126	125	128

(iii) Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 B.M. and that of Co^{2+} is 4.87 B.M. Why?

OR

Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?

LA Type Questions (5 marks)

22. (i) The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?
(ii) $E°$ of Cu is +0.34 V while that of Zn is −0.76 V. Explain.
(iii) When Cu^{2+} ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.

23. (i) The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?
(ii) Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?
(iii) What is actinoid contraction? What are the causes of actinoid contraction? Actinoid contraction has no consequence. Why?

24. (i) Explain why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium?
(ii) Why does copper not replace hydrogen from acids?
(iii) Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.

25. (i) How do the oxides of transition elements in lower oxidation states differ from those in higher oxidation states and why?
(ii) Why is $KMnO_4$ better bleaching agent than chlorine?
(iii) When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution is formed and when H^+ ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?

OR

(i) What is Lanthanoid contraction? Write down its two consequences?
(ii) Explain :
(a) Why is europium (II) more stable than cerium (II)?
(b) Why is +3 oxidation state of gadolinium (Z = 64) and lutetium (Z = 71) especially stable?

Detailed SOLUTIONS

1. (i) (a) : Oxide of V in lowest oxidation state, *i.e.*, VO is basic and ionic in character.

(ii) (a): Vanadyl ion is VO^{2+} where V is in +4 oxidation state.

(iii) (b) (iv) (c) (v) (a)

2. (b): Separation of Zr and Hf is difficult as both have same size due to lanthanide contraction.

3. (d): Actinoids possess greater tendency to form complexes as compared to lanthanoids because actinoid ions possess high charge and small size.

4. (d): Interstitial compounds are chemically inert.

5. (c) : $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$

OR

(b) : X^{3+} = [Ar]$3d^5$, X = [Ar]$3d^6\ 4s^2$ hence atomic number of element is 26.

6. (b): Cr^{3+} ($3d^3$) with 3 unpaired electrons

$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87$ B.M.

7. (c) : Tm (Thulium) is a lanthanoid.

8. (b) : Cu^{2+} has 1 unpaired electron in CuF_2, hence, it is coloured in solid state

$Cu^{2+} - 3d^9$

9. CuI_2 is not known because Cu^{2+} oxidises I^- to I_2.

$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$

10. Elements of group–11 (Cu, Ag, Au) are called coinage metals. They are so called because they were used in making coins.

11. After losing one electron Cr possesses half filled and Cu possesses fully filled *d*-orbital. So, it is difficult to remove an electron from it further. So, 2nd ionisation enthalpy of Cu and Cr are unexpectedly high.

$Cr^+ \rightarrow$ [Ar] $3d^5$

$Cu^+ \rightarrow$ [Ar] $3d^{10}$

12. Trivalent lanthanoids are coloured due to presence of *f*-electrons. The excitation of electron in *f*-level imparts colour to them. This colour is caused due to *f-f* transition. Some compounds show colour due to charge transfer also.

13. Due to lanthanoid contraction, the radii of elements of 4*d* and 5*d* series transition elements are almost same and hence they have similar physical properties.
(i) They occur in nature together.
(ii) Their separation is difficult.

14. The 5*f*-electrons are more effectively shielded from the nuclear charge than the 4*f*-electrons of lanthanoids. Because the outer electrons are less firmly held hence their ionisation enthalpy is low.

15. In laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

16. It changes to K_2MnO_4.

$2KMnO_4 \xrightarrow{513\ K} K_2MnO_4 + MnO_2 + O_2$

OR

This is due to extra stability of f^0, f^7 and f^{14} sub levels and almost identical energy of 5*f* and 6*d*- orbitals.

17. (i) (a) $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$
(b) $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
(ii) (a) Bleaching of wool.
(b) Decolourisation of oils.

18. If a substance absorbs wavelength corresponding to, red light, the transmitted light will consist of wavelengths corresponding to blue colour. The substance will, therefore, appear blue. The transmitted light has complementary colour to that of the absorbed light. Anhydrous cobalt (II) compounds absorb red light and transmit radiations of wavelength corresponding to blue colour (which is complementary to red colour), therefore, appear blue. The hydrated cobalt (II) compounds, however, absorb radiations of wavelengths corresponding to blue colour and, therefore, appear red.

19. The high melting and boiling points of transition metals are attributed to the involvement of greater number of electrons from $(n-1)$ *d*-orbital in addition to the *ns* electrons in the strong interatomic metallic bonding (*d-d* overlap).

20. The electronic configuration of Zn and Cu are :

Zn: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

From the above configuration, it is clear that first ionisation energy of Zn is greater than that of Cu (because of $4s^2$ and $4s^1$ configuration of Zn and Cu respectively). More energy is needed to remove an electron of $4s^2$ than that of $4s^1$.

The second *I.E.* of Cu is higher than that of Zn because for Cu^+ the configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ and for Zn^+ the configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$, it is easier to remove $4s^1$ electron of Zn^+ than a $3d$-electron from $3d^{10}$ (stable configuration).

OR

(i) (a) $6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

(b) $3Sn^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$

(ii) When dichromate ion is dissolved in alkali, it forms chromate ion and colour changes from orange to yellow.

$$\underset{\text{(orange)}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{(yellow)}}{2CrO_4^-} + H_2O$$

21. (i) $3d^5$ electronic configuration has highest number of unpaired electrons hence it has highest magnetic moment.

(ii) Cu will have highest density.

(iii) Due to symmetrically electronic configuration there is no orbital contribution in Cr^{3+} ion. However appreciable contribution takes place in Co^{2+} ion.

OR

Formation of Ce^{4+} is favoured by its noble gas configuration. Ce – $[Xe]4f^1\ 5d^1\ 6s^2$. Ce^{4+} becomes f^0 hence along with +3 oxidation state it also shows +4 O.S.

22. (i) Due to Lanthanoid contraction, the atomic radii of second and third row transition elements is almost same. So their properties are similar to each other much more as compared to first row elements.

(ii) In case of Zn, when two electrons are removed from $4s$ orbital, $3d^{10}$ configuration is acquired which is stable hence zinc undergoes oxidation with $E°$ value of –0.76 V. In case of Cu, the the sum of sublimation enthalpy and ionisation enthalpy to transform $Cu_{(s)}$ to $Cu^{2+}_{(aq)}$ is very high and is not balanced by its hydration enthalpy.

(iii) First cupric iodide is formed which decomposes to give cuprovs iodide and iodine.

$$CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

or $2Cu^{2+} + 4I^- \longrightarrow \underset{\text{White ppt.}}{Cu_2I_2} + I_2$

23. (i) As the oxidation state increases, size of the ion of transition element decreases. As per Fajan's rule, as the size of metal ion decreases, covalent character of bond formed increases.

(ii) The ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. It is due to the ability of oxygen to form multiple bonds with metals.

(iii) The gradual decrease in atomic radii from Actinium to Lawrencium is called actinoid contraction. This contraction is greater from element to element than the lanthanoid contraction resulting from poor shielding by $5f$-electrons. There is no consequence of actinoid contraction because elements succeeding actinoids are much less known.

24. (ii) $KMnO_4$ acts as an oxidising agent. It oxidises oxalic acid to CO_2 and itself gets reduced to Mn^{2+} ions which are colourless.

$$\underset{\text{Coloured}}{5C_2O_4^{2-}} + 2MnO_4^- + 16H^+ \rightarrow \underset{\text{Colourless}}{2Mn^{2+}} + 8H_2O + 10CO_2$$

(ii) Copper has a positive $E°$ value. It is below hydrogen in the reactivity series. It does not reduce H^+ of acids to H_2.

(iii) Due to regular increase in ionisation enthalpy the reactivity decreases along the row.

25. (i) In the lower oxidation state, the transition metal oxides are basic and they are acidic if the metal is in higher oxidation state. The oxides are amphoteric when the metal is in intermediate oxidation state.

For example,

$$\overset{+3}{Mn_2O_3}\ \underset{\text{Basic}}{} \qquad \overset{+4}{MnO_2}\ \underset{\text{Amphoteric}}{} \qquad \overset{+7}{Mn_2O_7}\ \underset{\text{Acidic}}{}$$

In case of lower oxide of a transition metal, the metal atom has a low oxidation state. This means some of the valence electrons of the metal atom are not involved in bonding, hence, these can be used for donation. Thus, these are act as bases.

(ii) Chlorine may form some harmful compounds during bleaching of textiles. These compounds may cause water pollution whereas the bleaching by $KMnO_4$ is harmless.

(iii) On treating with alkalies dichromate ions are converted to chromate ions which are yellow in colour. On acidifying yellow colour again changes to orange.

$$\underset{\text{Dichromate (orange)}}{Cr_2O_7^{2-}} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{Chromate (yellow)}}{CrO_4^{2-}}$$

OR

(i) **Lanthanoid contraction :** The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by $4f$-electrons.

Consequences of lanthanoid contraction :

(a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(b) Atomic and ionic sizes of $4d$ transition series elements and $5d$ series elements are similar. *e.g.*, atomic radii of zirconium(Zr) is same as that of hafnium Hf.

(ii) (a) Europium (II) has electronic configuration $[Xe]4f^7 5d^0$ while cerium (II) has electronic configuration $[Xe]4f^1 5d^1$. In Eu^{2+}, $4f$ subshell is half filled and $5d$-subshell is empty. Since half filled and completely filled electronic configurations are more stable, hence Eu^{2+} ions is more stable than Ce^{2+}.

(b) This is because gadolinium in +3 state has half filled $4f$-subshell ($4f^7$) and lutetium in +3 state has completely filled $4f$-subshell which are very stable configurations.

CHAPTER

5

Coordination Compounds

TOPICS

5.1 Werner's Theory of Coordination Compounds

5.2 Definition of Some Important Terms Pertaining to Coordination Compounds

5.3 Nomenclature of Coordination Compounds

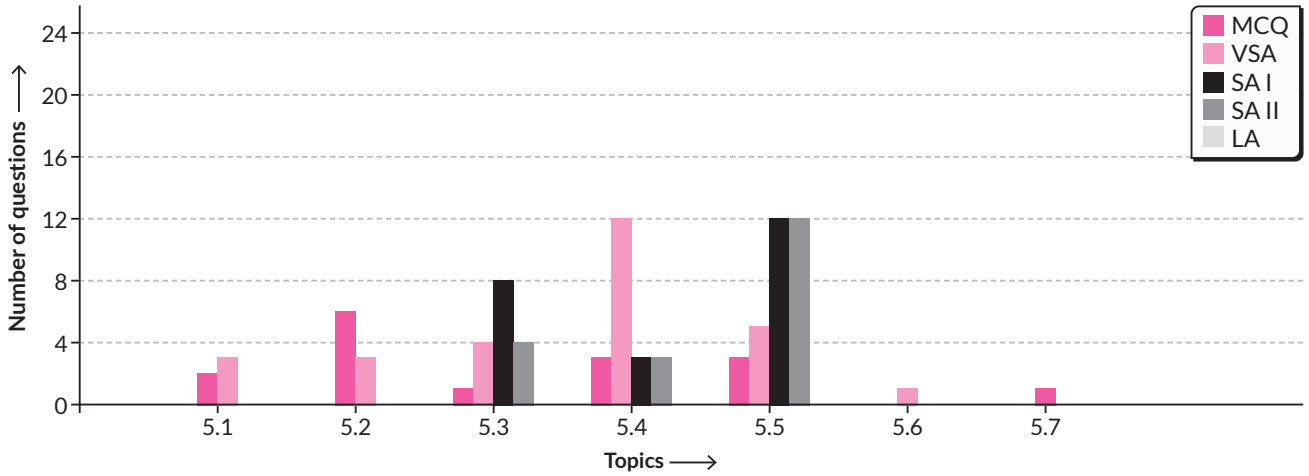
5.4 Isomerism in Coordination Compounds

5.5 Bonding in Coordination Compounds

5.6 Bonding in Metal Carbonyls

5.7 Importance and Applications of Coordination Compounds

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

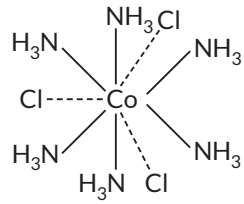
- Topics 5.3, 5.4 and 5.5 are highly scoring topics.
- Maximum total weightage is of Topic 5.5 *Bonding in Coordination Compounds*.
- Maximum VSA type questions were asked from Topic 5.4 *Isomerism in Coordination Compounds*.
- Maximum SA I and SA II type questions were asked from Topic 5.5 *Bonding in Coordination Compounds*.

QUICK RECAP

Werner's coordination theory :

- It explains the nature of bonding in complexes. Metals show two different kinds of valencies :
  - **Primary valency :** Non-directional and ionisable. It is equal to the oxidation state of the central metal ion.
  - **Secondary valency :** Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or sometimes by positively charged ligands.
- The ionisation of the coordination compound is written as :

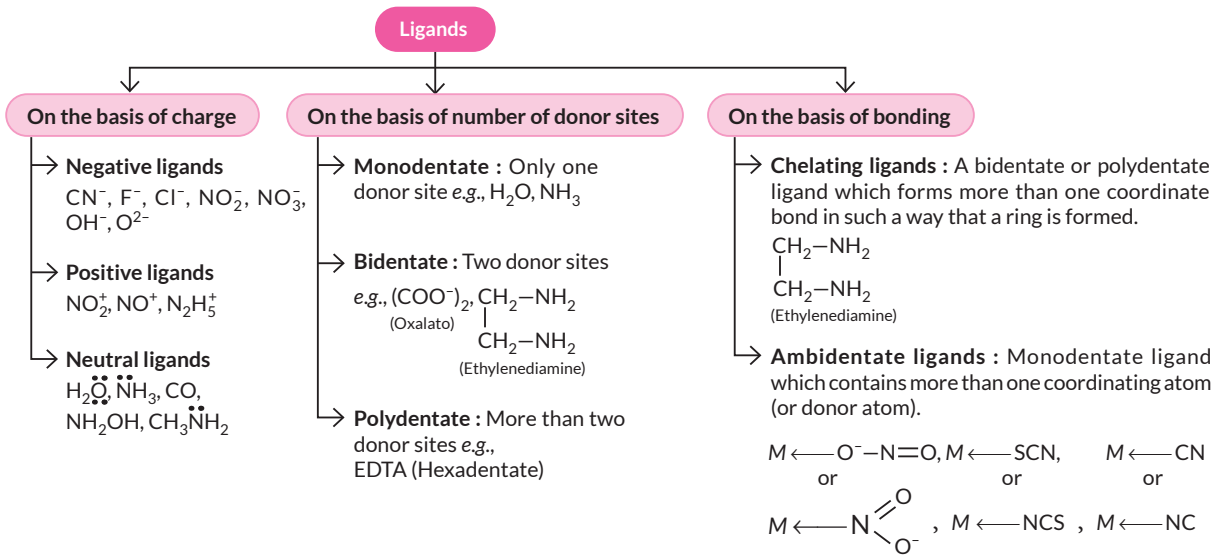
$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$



$[Co(NH_3)_6]Cl_3$

Representaion of $CoCl_3 \cdot 6NH_3$ complex according to Werner's theory

- **Addition compounds :** The compounds formed by combination of two or more simple compounds are called *addition compounds*. They are of two types :
  - **Double salt :** A compound formed by combination of two or more simple compounds, which is stable in solid state only is called *double salt*. In solution, it breaks into its component ions.
    e.g., $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; Potash alum
    $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$; Mohr's salt
    $KCl \cdot MgCl_2 \cdot 6H_2O$; Carnallite
  - **Complex compound :** A compound formed by combination of two or more simple compounds which retain its identity both in solid and solution states is called *complex compound*.
    e.g., $K_4[Fe(CN)_6]$; Potassium ferrocyanide
    $[Cu(NH_3)_4]SO_4$; Cupramine sulphate
- **Some important terms pertaining to coordination compounds :**
  - **Coordination entity :** The central metal atom or ion and ligands taken together is called *coordination entity*. It may be positive, negative or neutral.
    e.g., $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{4-}$, $[Ni(CO)_4]$
  - **Central atom :** The atom or ion with which definite number of ligands are attached in a definite geometry is called *central atom/ion*. Any atom/ion which has high positive charge density or vacant orbitals of suitable energy may be central atom or ion, *e.g.*, transition metals, lanthanoids. It is a Lewis acid (electron acceptor).
  - **Ligands :** Molecules or ions which are bound to the central atom/ion in the coordination entity are called *ligands*. A molecule or ion which has high negative charge or dipole or lone pair of electrons may be ligands. It is a Lewis base (electron donor).
  - **Classification of ligands :**

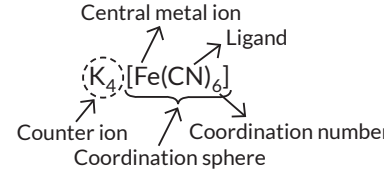

Ligands
On the basis of charge
On the basis of number of donor sites
On the basis of bonding
Negative ligands
CN⁻, F⁻, Cl⁻, NO2⁻, NO3⁻, OH⁻, O2⁻
Positive ligands
NO2+, NO+, N2H5+
Neutral ligands
H2O, NH3, CO, NH2OH, CH3NH2
Monodentate : Only one donor site e.g., H2O, NH3
Bidentate : Two donor sites
e.g., (COO⁻)2, CH2—NH2, CH2—NH2
(Oxalato)
(Ethylenediamine)
Polydentate : More than two donor sites e.g., EDTA (Hexadentate)
Chelating ligands : A bidentate or polydentate ligand which forms more than one coordinate bond in such a way that a ring is formed.
CH2—NH2, CH2—NH2
(Ethylenediamine)
Ambidentate ligands : Monodentate ligand which contains more than one coordinating atom (or donor atom).
M ← O⁻—N=O, M ← SCN, M ← CN
or or or
M ← N(=O)O⁻ , M ← NCS , M ← NC

  - **Coordination number (C.N.) :** The total number of coordinate bonds through which the central metal atom or ion is attached with ligands is known as coordination number.
    Examples : $[Ag(CN)_2]^-$: C.N. = 2,
    $[Cu(NH_3)_4]^{2+}$: C.N. = 4,
    $[Cr(H_2O)_6]^{3+}$: C.N. = 6
  - **Coordination sphere :** The central atom and the ligands which are directly attached are collectively known as coordination sphere. It is non-ionisable and written enclosed in square brackets. The ionisable groups are written outside the brackets.

Example :

$$[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

Coordination sphere — Ionisable group



- **Coordination polyhedron :** The spatial arrangement of the ligand atoms which are directly attached to the central atom defines a coordination polyhedron about the central atom, *e.g.*, $[(Co(NH_3)_6]^{2+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral. Octahedral is most common coordination polyhedron.

Homoleptic and heteroleptic complexes :

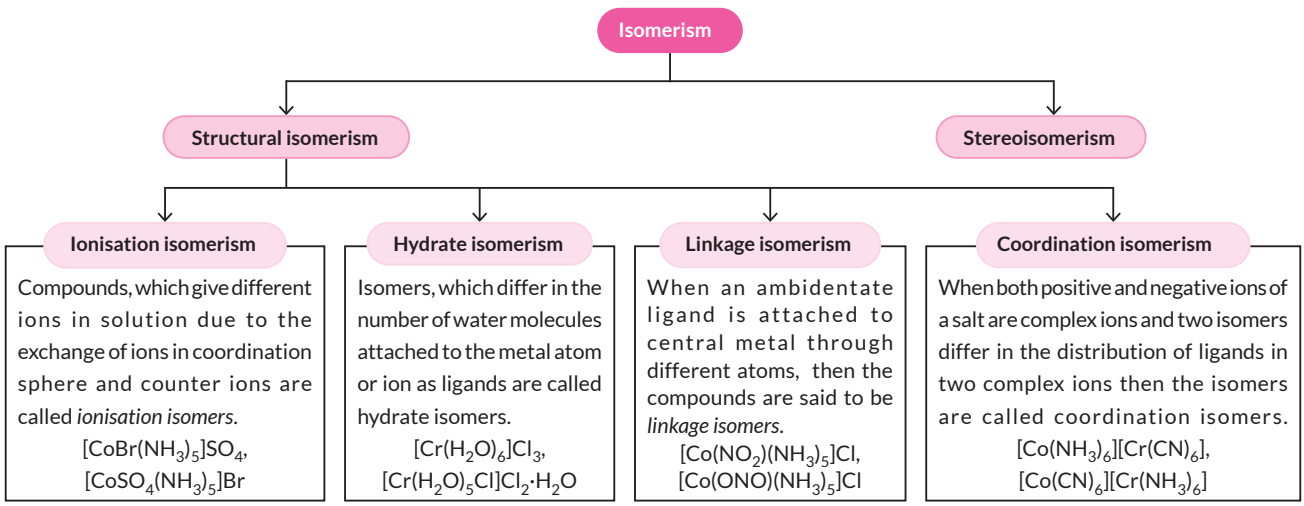
- **Homoleptic complexes :** Complexes in which a metal is bound to only one kind of ligands are called *homoleptic complexes*.
  e.g., $[Co(NH_3)_6]^{3+}$, $[Ti(H_2O)_6]^{3+}$, $[Cu(CN)_4]^{3-}$
- **Heteroleptic complexes :** Complexes in which the central atom is bound to different types of ligands are called *heteroleptic complexes*.
  e.g., $[Co(NH_3)_4Cl_2]$, $K_2[Fe(CN)_5NO]$, $[Fe(H_2O)_5NO]SO_4$

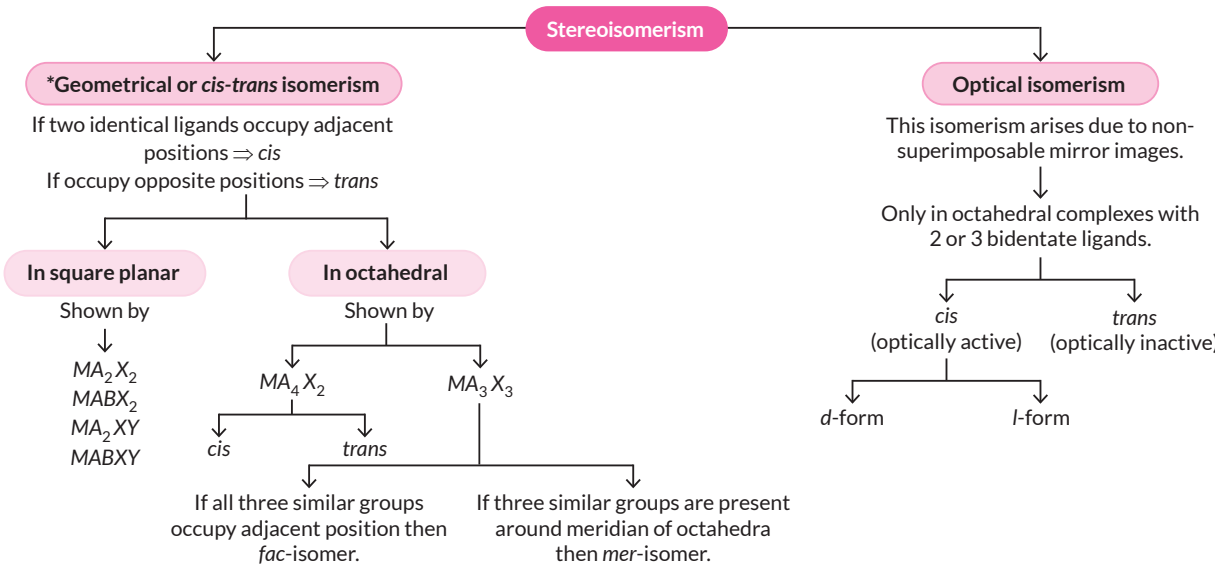
Nomenclature of coordination compounds :

- **Rules for writing the formula of coordination compounds :**
  - Formula of the cation whether simple or complex must be written first, followed by anion.
  - The coordination sphere is written in square brackets.
  - Within the coordination sphere the sequence of symbols is, first the metal atom followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically.
  - Polyatomic ligands are enclosed in parentheses.
  - The number of cations or anions to be written in the formula is calculated on the basis that total positive charge must be equal to the total negative charge, as the complex as a whole is electrically neutral.

- **Rules for naming coordination compounds :**
  - The cation is named first then the anion.
  - In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
  - The complex part is written as one word.
  - When the coordination sphere is anionic, name of central metal ends in *–ate*.
- **Naming of ligands :**
  - Name of anionic ligands end in *–o*.
    e.g., Cl^- : Chlorido
  - Neutral ligands (with a few exceptions) retain their names *e.g.*, NH_3 : Ammine
  - Name of cationic ligands end in – *ium*. *e.g.*, NO_2^+ : Nitronium
  - Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae. *e.g.*, ethylenediamine(*en*).
  - Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.
    e.g., $-SCN^-$ (Thiocyanato-S or Thiocyanato), $-NCS^-$ (Thiocyanato-N or Isothiocyanato),
    $-ONO^-$ (Nitrito-O or Nitrito),
    $-NO_2^-$ (Nitrito-N or Nitro)
  - The prefixes *di-*, *tri-*, *tetra-*, *penta-* and *hexa-* are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by *bis*-(2), *tris*-(3), *tetrakis*-(4), *pentakis*-(5) and *hexakis*-(6).

Isomerism : Two or more substances having the same molecular formula but different structural or spatial arrangement are called *isomers* and phenomenon is called *isomerism*.


Isomerism
Structural isomerism
Stereoisomerism
Ionisation isomerism
Compounds, which give different ions in solution due to the exchange of ions in coordination sphere and counter ions are called *ionisation isomers*.
$[CoBr(NH_3)_5]SO_4$, $[CoSO_4(NH_3)_5]Br$
Hydrate isomerism
Isomers, which differ in the number of water molecules attached to the metal atom or ion as ligands are called hydrate isomers.
$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
Linkage isomerism
When an ambidentate ligand is attached to central metal through different atoms, then the compounds are said to be *linkage isomers*.
$[Co(NO_2)(NH_3)_5]Cl$, $[Co(ONO)(NH_3)_5]Cl$
Coordination isomerism
When both positive and negative ions of a salt are complex ions and two isomers differ in the distribution of ligands in two complex ions then the isomers are called coordination isomers.
$[Co(NH_3)_6][Cr(CN)_6]$, $[Co(CN)_6][Cr(NH_3)_6]$



(* Geometrical isomerism is not shown by tetrahedral complexes.)

Bonding in coordination compounds :

- **Valence Bond Theory (VBT) :** It was developed by Pauling.
  - A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bonds with the ligands.
  - Central metal ion can use appropriate number of *s*-, *p*- or *d*-orbitals for hybridisation depending upon the total number of ligands.
  - The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.

C. No.	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, where, $X = Cl^-, Br^-, I^-$
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

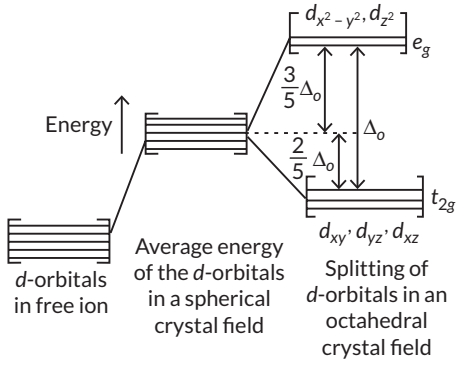
Inner orbital complexes	Outer orbital complexes
Involves inner *d*-orbitals *i.e.*, $(n-1)d$-orbitals.	Involves outer *d*-orbitals *i.e.*, *nd*-orbitals.
Low spin complexes	High spin complexes
Have less or no unpaired electrons. *e.g.*, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{4-}$	Have large number of unpaired electrons. *e.g.*, $[MnF_6]^{3-}$, $[CoF_6]^{3-}$

- Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
- Paramagnetism ∝ No. of unpaired electrons.
- Magnetic moment $= \sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons.

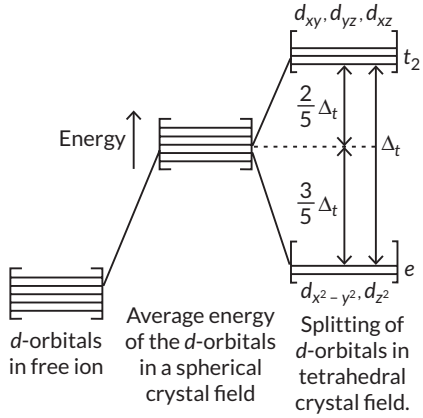
- **Crystal Field Theory (CFT) :** It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and

results in splitting, which depends upon nature of ligand field strength.

- Greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.
- Crystal field splitting in octahedral coordination complexes is shown as :



- If $\Delta_o < P$ (where 'P' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.
- If $\Delta_o > P$, then pairing of electrons takes place and a low spin complex is formed.
- Crystal field splitting in tetrahedral complexes is shown as :



- Difference in energy between e and t_2 level is less in tetrahedral complexes.

$$\Delta_t = \frac{4}{9}\Delta_o$$

- **Spectrochemical series :** Arrangement of ligands in the order of increasing field strength.

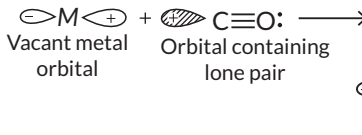
Weak field ligands → Increasing order of CFSE (Δ) → Strong field ligands

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O$
$< NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

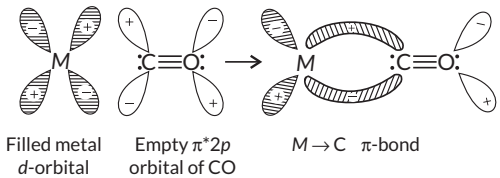
Colour of coordination compounds : The magnitude of CFSE (Δ) for most of the complexes is of the same order as the energy of a photon of visible light. Hence, whenever *d-d* transition takes place, it imparts colour to the complex. The colour of the complex is the colour complementary to the wavelength absorbed.

Bonding in metal carbonyls :

- Metal–carbon bond in metal carbonyls possesses both σ- and π-characters.
- Its formation involves the following steps :
- Donation of lone pair of electrons of CO to suitable empty metal *d*-orbital resulting in the formation of sigma bond.



- π-Overlap involving filled metal *d*-orbital with an empty antibonding π^*2p orbital of same CO. This results in formation of $M \rightarrow C$ π-bond. This is also called *back bonding*.



Applications of coordination compounds :

- Coordination compounds are of great importance in biological system. *e.g.*, chlorophyll, haemoglobin, vitamin B_{12}, etc. are coordination compounds of Mg, Fe and Co respectively.
- Coordination compounds are used for qualitative and quantitative analysis, extraction of metals, electroplating, photography and as dyes.
- *cis*-Platin is used in cancer treatment, EDTA is often used for treatment of lead poisoning.
- Coordination compounds are used as catalysts for many industrial processes. Example include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.

COORDINATION COMPOUNDS

Metal atoms are bound to many anions or neutral molecules. Structure first formulated by Alfred Werner.

Primary valence (ionisable) : Oxidation state of central metal atom.
Secondary valence (non-ionisable) : No. of groups bound directly to the metal ion (coordination number).

Important Terms

- **Coordination entity :** Central metal atom/ion + bonded ions/ molecules.
- **Central atom/ion :** Lewis acids.
- **Ligands :** Ions/molecules bound to central atom/ion.
- **Coordination number :** Number of ligands or donor atoms bonded directly to metal.
- **Coordination sphere :** Central metal atom/ion + attached ligands enclosed in square bracket.
- **Coordination polyhedron :** Spatial arrangement of ligands.
- **Oxidation no. of central atom :** Charge that it would carry if all ligands are removed along with their shared electron pairs.

Isomerism

Structural

- **Linkage :** in those having ambidentate ligand.
- **Coordination :** by interchange of ligands.
- **Ionisation :** Counter ion displaces the potential ligand.
- **Solvate or hydrate :** Solvent molecule present differently (directly bonded or free).

Stereoisomerism

Geometrical : Different possible geometrical arrangement of the ligands.

- In square planar → *cis* and *trans*
- In octahedral
  - **Facial :** Three donor atoms of the same ligands occupy adjacent position at the corners of the octahedral face.
  - **Meridional :** Occupies the Meridian of the octahedron.

Optical : Non-superimposable mirror images → enantiomers and chiral.

- **Dextro (*d*) :** Rotate the plane of polarised light to right
- **Laevo (*l*) :** Rotate the plane of polarised light to left

Bonding

Spectrochemical series : Arrangement of ligands in the order of increasing field strength.
$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$.
If $\Delta_o < P$, then complex is high spin.
If $\Delta_o > P$, then complex is low spin. $\Delta_t = 4/9\Delta_o$

Valence Bond Theory

Under the influence of ligands hybridised orbitals $[(n-1)d, ns, np]$ or $[ns, np, nd]$ overlap with ligand orbitals.

- **Inner orbital complex :** Low spin or spin paired complex. Uses 3*d* orbital in hybridisation.
- **Outer orbital complex :** High spin or spin free complex. Uses 4*d* orbital in hybridisation.

Crystal Field Theory

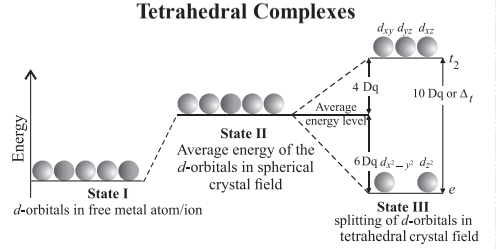
Metal-ligand bond considered as ionic, under ligand's influence, *d*-orbitals are splitted into two levels with energy difference Δ_o or Δ_t

In tetrahedral complexes:
$\frac{\text{energy of } t_2}{(d_{xy}, d_{yz}, d_{xz})}$
$\frac{\text{energy of } e}{(d_{x^2-y^2}, d_{z^2})}$
$\Delta_t = \frac{4}{9}\Delta_o$

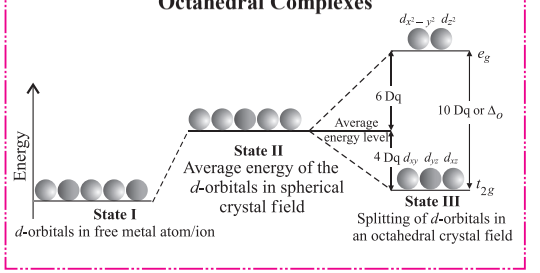
In octahedral complexes:
$\frac{\text{energy of } e_g}{(d_{x^2-y^2}, d_{z^2})}$
$\frac{\text{energy of } t_{2g}}{(d_{xy}, d_{yz}, d_{xz})}$

Crystal field splitting energy (CFSE) = $(-0.4x + 0.6y)\Delta_o$
where, x = no. of e^-s in t_{2g} orbitals
y = no. of e^-s in e_g orbitals.

Tetrahedral Complexes



Octahedral Complexes



BRAIN MAP

Previous Years' CBSE Board Questions

5.1 Werner's Theory of Coordination Compounds

MCQ

1. **Assertion :** $[Co(NH_3)_5SO_4]Cl$ gives a white precipitate with silver nitrate solution.
Reason : The complex dissociates to give Cl^- and SO_4^{2-} ions.
(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is true, but Reason (R) is false.
(d) Assertion (A) is false, but Reason (R) is true. *(2023)*

2. One mole of $CrCl_3 \cdot 6H_2O$ compound reacts with excess $AgNO_3$ solution to yield two moles of $AgCl_{(s)}$. The structural formula of the compound is
(a) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (b) $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$
(c) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (d) $[Cr(H_2O)_6Cl_3]$ *(2020)*

VSA (1 mark)

3. When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex. *(AI 2019, 1/2, Delhi 2016)*

4. What is the difference between a complex and a double salt? *(AI 2019)* R

5. When a coordination compound $CoCl_3 \cdot 6NH_3$ is mixed with $AgNO_3$, 3 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex. *(1/2, AI 2016)*

5.2 Definition of Some Important Terms Pertaining to Coordination Compounds

MCQ

6. The oxidation number of Co in $[Co(en)_3]_2(SO_4)_3$ is
(a) +2 (b) +3 (c) +4 (d) +6
(2021C) Ap

7. Which of the following ligands form a 'chelate' complex with metal ion ?
(a) H_2O (b) CN^- (c) $C_2O_4^{2-}$ (d) Cl^-
(2021C)

8. The coordination number of Cr in $[CrCl_2(ox)_2]^{3-}$ is
(a) 6 (b) 5 (c) 4 (d) 3
(2021C)

9. The coordination number of 'Co' in the complex $[Co(en)_3]^{3+}$ is
(a) 3 (b) 6 (c) 4 (d) 5
(2020) R

10. **Assertion (A) :** $[Pt(en)_2Cl_2]^{2+}$ complex is less stable than $[Pt(NH_3)_4Cl_2]^{2+}$ complex.
Reason (R) : $[Pt(en)_2Cl_2]^{2+}$ complex shows chelate effect.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

11. The oxidation state of Ni in $[Ni(CO)_4]$ is
(a) 0 (b) 2
(c) 3 (d) 4 *(2020)* An

VSA (1 mark)

12. Amongst $[Fe(C_2O_4)_3]^{3-}$ and $[Fe(NH_3)_6]^{3+}$, which is more stable and why? *(2019C)*

13. Write the coordination number and oxidation state of platinum in the complex $[Pt(en)_2Cl_2]$. *(2018)*

14. Which of the following is more stable complex and why?
$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ *(Delhi 2014)*

5.3 Nomenclature of Coordination Compounds

MCQ

15. The formula of the coordination compound tetraamminechloridonitrito-N-cobalt(III) chloride is :
(a) $[Co(NH_3)_4Cl(ONO)]Cl_2$
(b) $[Co(NH_3)_4Cl_2(NO_2)]Cl$
(c) $[Co(NH_3)_4Cl(NO_2)]Cl$
(d) $[Co(NH_3)_4(NO_2)]Cl_3$ *(2021C)*

VSA (1 mark)

16. Write the formula of the following coordination compound :
Iron(III) hexacyanidoferrate(II) *(1/3, 2018)*

17. Write the IUPAC name of the following complex : $[Cr(NH_3)_3Cl_3]$. *(1/3, Delhi 2017)*

18. Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]Cl$. *(1/3, Delhi 2017)*

19. When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write IUPAC name of the complex. *(1/2, Delhi 2016)* An

SA I (2 marks)

20. Give the formulae of the following compounds :
(a) Potassium tetrahydroxidozincate(II)
(b) Hexaammineplatinum(IV) chloride *(2020)* Ap

21. Using IUPAC norms write the formulae for the following :
(i) Pentaamminenitrito–O–cobalt(III) chloride
(ii) Potassium tetracyanidonickelate(II)
(NCERT, Delhi 2019)

22. Using IUPAC norms write the formulae for the following :
(a) Sodium dicyanidoaurate(I)
(b) Tetraamminechloridonitrito-N-platinum(IV) sulphate *(AI 2017)*

23. Using IUPAC norms write the formulae for the following :
(a) *Tris*(ethane-1,2,diamine)chromium(III) chloride
(b) Potassium tetrahydroxozincate(II) *(AI 2017)*

24. Using IUPAC norms write the formulae for the following :
(a) Potassium trioxalatoaluminate(III)
(b) Dichlorido*bis*(ethane-1,2-diamine)cobalt(III)
(AI 2017) Ap

25. (i) Write down the IUPAC name of the following complex :
$[Cr(NH_3)_2Cl_2(en)]Cl$ (*en* = ethylenediamine)
(ii) Write the formula for the following complex :
Pentaamminenitrito-O-cobalt (III). *(Delhi 2015)*

26. Using IUPAC norms write the formulae for the following coordination compounds :
(i) Hexaamminecobalt(III) chloride
(ii) Potassium tetrachloridonickelate(II) *(AI 2015)*

27. (i) Write down the IUPAC name of the following complex : $[Cr(en)_3]Cl_3$.
(ii) Write the formula for the following complex : Potassium trioxalatochromate(III).
(Foreign 2015)

SA II (3 marks)

28. (i) Write the IUPAC name of the following complex : $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(ii) What is the difference between an Ambidentate ligand and a Bidentate ligand ?
(iii) Out of $[Fe(NH_3)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$, which complex is more stable and why?
(Term II, 2021-22) U

29. Write the IUPAC name of the following :
(i) $[Co(NH_3)_6]Cl_3$ (ii) $[NiCl_4]^{2-}$
(iii) $K_3[Fe(CN)_6]$ *(AI 2015C)* Ap

30. Write down the IUPAC name for each of the following complexes :
(i) $[Co(NH_3)_5Cl]Cl_2$ (ii) $K_3[Fe(CN)_6]$
(iii) $[NiCl_4]^{2-}$ *(Delhi 2014C)* U

31. Write the IUPAC name and draw the structure of each of the following complex entities :
(i) $\left[Co\begin{pmatrix}COO\\|\\COO\end{pmatrix}_3\right]^{3-}$ (ii) $[Cr(CO)_6]$
(iii) $[PtCl_3(C_2H_4)]^-$
(At. nos. Cr = 25, Co = 27, Pt = 78) *(AI 2014C)* Cr

5.4 Isomerism in Coordination Compounds

Structural Isomerism

MCQ

32. The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(Br)(NH_3)_5]SO_4$ represent
(a) optical isomerism
(b) linkage isomerism
(c) ionisation isomerism
(d) coordination isomerism. *(2023)*

33. The pair $[Co(NH_3)_4Cl_2]Br_2$ and $[Co(NH_3)_4Br_2]Cl_2$ will show
(a) linkage isomerism
(b) hydrate isomerism
(c) ionization isomerism
(d) coordinate isomerism *(2020)* U

34. **Assertion (A) :** Linkage isomerism arises in coordination compounds because of ambidentate ligand.
Reason (R) : Ambidentate ligand like NO_2 has two different donor atoms *i.e.*, N and O.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

VSA (1 mark)

35. What type of isomerism is shown by the complex $[Co(NH_3)_5NO_2]Cl_2$? *(2020)*

36. What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$? *(1/3, 2018)*

OR

What type of isomerism is exhibited by the following complex : $[Co(NH_3)_5SO_4]Cl$ *(Foreign 2014)*

37. What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?
(1/3, Delhi 2017, Foreign 2014)

38. What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$? *(1/3, AI 2017)*

39. What type of isomerism is exhibited by the complex $[Co(NH_3)_5NO_2]^{2+}$? *(Foreign 2014)*

SA I (2 marks)

40. (a) Which of the following species cannot act as a ligand? Give reason.
OH^-, NH_4^+, CH_3NH_2, H_2O
(b) The complex $[Co(NH_3)_5(NO_2)]Cl_2$ is red in colour. Give IUPAC name of its linkage isomer.
(2023)

Stereoisomerism

VSA (1 mark)

41. What type of isomerism is shown by the complex $[Co(en)_2Cl_2]^+$? Name the structure of an isomer of this complex which is optically active. *(1/2, 2020)* An

42. What type of isomerism is shown by the complex $[Co(en)_3]Cl_3$? *(NCERT Intext, 1/3, Delhi 2017)*

OR

What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? (*en* = ethane-1,2-diamine) *(1/3, AI 2014)*

43. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically active.
(1/3, Delhi 2016)

44. Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive. *(AI 2016)*

45. Draw the geometrical isomers of complex $[Pt(NH_3)_2Cl_2]$. *(1/3, Delhi 2015)*

46. Write down the IUPAC name of the complex $[Pt(en)_2Cl_2]^{2+}$. What type of isomerism is shown by this complex? *(AI 2015)*

47. Draw the geometrical isomers of complex $[Pt(en)_2Cl_2]^{2+}$. *(1/3, Foreign 2015)* Cr

SA I (2 marks)

48. Write IUPAC name of the complex $[Pt(en)_2Cl_2]$. Draw structures of geometrical isomers for this complex. *(2019)*

49. Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex. *(Delhi 2019)*

SA II (3 marks)

50. Indicate the types of isomerism exhibited by the following complexes :
(i) $[Co(NH_3)_5(NO_2)]^{2+}$
(ii) $[Co(en)_3]Cl_3$ (*en* = ethylene diamine)
(iii) $[Pt(NH_3)_2Cl_2]$ *(Delhi 2015C)* U

51. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit? *(Delhi 2014)*

52. Draw the structures of optical isomers of each of the following complex ions :
$[Cr(C_2O_4)]^{3-}$, $[PtCl_2(en)_2]^{2+}$, $[Cr(NH_3)_2Cl_2(en)]^+$
(Delhi 2014C)

5.5 Bonding in Coordination Compounds

Valence Bond Theory

MCQ

53. The magnetic moment of $[NiCl_4]^{2-}$ is
(a) 1.82 B.M. (b) 2.82 B.M.
(c) 4.42 B.M. (d) 5.46 B.M.
[Atomic number : Ni = 28] *(2023)*

VSA (1 mark)

54. Write the IUPAC name and hybridisation of the complex, $[CoF_6]^{3-}$.
(Given : Atomic number of Co = 27) *(1/2, 2020)*

OR

Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) *(1/3, 2018)*

55. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion. *(2019C)* An

56. Write the hybridisation and magnetic character of $[Co(C_2O_4)_3]^{3-}$.
(At. no. of Co = 27) *(1/3, Delhi 2017)*

57. Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. no. : Cr = 24, Co = 27, Ni = 28)
(NCERT Intext, 1/3, AI 2014)

SA I (2 marks)

58. (i) Write the IUPAC name of $[Mn(H_2O)_6]SO_4$.
(ii) Why is $[Fe(CN)_6]^{4-}$ diamagnetic while $[FeF_6]^{3-}$ is paramagnetic ? [At. No. Fe= 26] *(2021C)*

59. Write IUPAC name and hybridization of the following complexes :
(i) $[Ni(CO)_4]$
(ii) $[CoF_6]^{3-}$
(Atomic number Ni = 28, Co = 27) *(2020)* Ap

60. (a) Write the IUPAC name and hybridisation of the complex $[Fe(CN)_6]^{3-}$.
(Given : Atomic number of Fe = 26)
(b) What is the difference between an ambidentate ligand and a chelating ligand ? *(2020)* Ap

61. Out of $[CoF_6]^{3-}$ and $[Co(en)_3]^{3+}$, which one complex is
(i) paramagnetic (ii) more stable
(iii) inner orbital complex and
(iv) high spin complex
(Atomic no. of Co = 27) *(2019)*

62. Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is
(i) diamagnetic
(ii) more stable
(iii) outer orbital complex and
(iv) low spin complex ?
(Atomic no. of Co = 27) *(Delhi 2019)*

63. For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridization, magnetic character and spin of the complex. (At. number Fe = 26) *(2/3,AI 2016)*

64. Write the hybridization and shape of the following complexes :
(i) $[CoF_6]^{3-}$
(ii) $[Ni(CN)_4]^{2-}$
(Atomic number : Co = 27, Ni = 28) *(AI 2015)*

65. Write the state of hybridization, shape and IUPAC name of the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) *(Foreign 2014)*

66. Write the state of hybridization, shape and IUPAC name of the complex $[Ni(CN)_4]^{2-}$. (Atomic no. of Ni = 28) *(Foreign 2014)*

67. Write the state of hybridization, shape and IUPAC name of the complex $[Co(NH_3)_6]^{3+}$. (Atomic no. of Co = 27) *(Foreign 2014)*

SA II (3 marks)

68. (a) On the basis of crystal field theory, write the electronic configuration for d^4 with a strong field ligand for which $\Delta_o > P$.
(b) A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CO)_4]$ is colourless. Explain.
[Atomic number : Ni = 28] *(2023)*

69. (a) Write the hybridisation, shape and magnetic character of $[CoF_6]^{3-}$.
[Atomic number of Co = 27]
(b) Write the formula of pentaamminechloridocobalt(III) chloride. *(Term II, 2021-22)* Ev

70. (i) Calculate the spin only magnetic moment of the complex $[FeF_6]^{3-}$. (Atomic number of Fe = 26)
(ii) Write the IUPAC name of the given complex : $[Co(NH_3)_5Cl]Cl_2$
(iii) Why is the complex $[Co(en)_3]^{3+}$ more stable than $[CoF_6]^{3-}$? *(Term II, 2021-22)* Ev

71. (a) Using valence bond theory, predict the hybridization and magnetic character of the complex : $[Ni(CO)_4]$ (Atomic number : Ni = 28)
(b) Write IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$.
(c) Why $[Co(en)_3]^{3+}$ is a more stable complex than $[Co(NH_3)_6]^{3+}$? *(Term II, 2021-22)* Ev

72. Write the hybridisation and magnetic character of the following complexes :
(i) $[Fe(H_2O)_6]^{2+}$
(ii) $[Ni(CN)_4]^{2-}$
[Atomic number : Fe = 26, Ni = 28] *(AI 2019)*

LA (5 marks)

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

73. In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape of the complexes.
(i) If $PtCl_2.2NH_3$ does not react with $AgNO_3$, what will be its formula?
(ii) What is the secondary valency of $[Co(en)_3]^{3+}$?
(iii) (1) Write the formula of Iron(III)hexacyanidoferrate(II)
(2) Write the IUPAC name of $[Co(NH_3)_5Cl]Cl_2$.
OR
(iii) Write the hybridization and magnetic behaviour of $[Ni(CN)_4]^{2-}$. *(2023)*

Crystal Field Theory

MCQ

74. **Assertion (A) :** Low spin tetrahedral complexes are rarely observed.
Reason (R) : Crystal field splitting energy is less than pairing energy for tetrahedral complexes.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is wrong statement.
(d) Assertion (A) is wrong, but Reason (R) is correct statement. *(2023, 2020)* R

75. The crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complexes is related as
(a) $\Delta_t = \frac{2}{9}\Delta_o$ (b) $\Delta_t = \frac{5}{9}\Delta_o$
(c) $\Delta_t = \frac{4}{9}\Delta_o$ (d) $\Delta_t = 2\,\Delta_o$ *(2020)*

VSA (1 mark)

76. Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless?
(At. no. of Ni = 28) *(NCERT, 1/3, Delhi 2017)* Ev

SA I (2 marks)

77. (a) Why is $[NiCl_4]^{2-}$ paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic?
(Atomic number of Ni = 28)
(b) Why are low spin tetrahedral complexes rarely observed? *(2/3, AI 2017)* An

78. (i) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_o < P$.
(ii) Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$.
(At. no. of Ni = 28) *(2/3, Delhi 2015)* An

SA II (3 marks)

79. (i) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$.
(ii) Using valence bond theory, predict the hybridization and magnetic character of $[Ni(CN)_4]^{2-}$. (Atomic number of Ni = 28)

(iii) Write the formula of the following complex using IUPAC norms : Dichloridobis (ethane-1,2-diamine) cobalt (III) *(Term II, 2021-22)*

80. (i) Write the electronic configuration of d^4 on the basis of crystal field splitting theory, if $\Delta_o < P$.
(ii) $[Ni(CN)_4]^{2-}$ with square-planar structure is diamagnetic and $[NiCl_4]^{2-}$ with tetrahedral geometry is paramagnetic. Give reason to support the statement.
[Atomic number : Ni = 28]
(iii) Write the number of ions produced in the solution from the following complex :
$[PtCl_2(NH_3)_4]Cl_2$ *(Term II, 2021-22)* Ap

81. (a) Write the IUPAC name of the following complex : $K_3[Cr(C_2O_4)_3]$
(b) On the basis of crystal field theory, write the electronic configuration of d^5 ion if $\Delta_o < P$.
(c) What are ambidentate ligands?
(Term II, 2021-22)

82. (i) Write the IUPAC name of the following complex : $K_2[PdCl_4]$
(ii) Using crystal field theory, write the electronic configuration of d^5 ion, if $\Delta_o > P$.
(iii) What are homoleptic complexes ?
(Term II, 2021-22)

83. (i) Why chelate complexes are more stable than complexes with unidentate ligands?
(ii) What is "spectrochemical series"? What is the difference between a weak field ligand and a strong field ligand ? *(Term II, 2021-22)*

84. (a) Give the IUPAC name and electronic configuration of central metal atom in terms of t_{2g} and e_g of $K_4[Mn(CN)_6]$.
(b) What is meant by 'Chelate effect' ? Give an example. *(2020)* U

85. Define the following :
(a) Ambidentate ligands
(b) Spectrochemical series
(c) Heteroleptic complexes *(2019C)*

5.6 Bonding in Metal Carbonyls

VSA (1 mark)

86. Out of NH_3 and CO, which ligand forms a more stable complex with a transition metal and why?
(1/3, AI 2015) U

5.7 Importance and Applications of Coordination Compounds

MCQ

87. **Assertion (A) :** EDTA is used to determine hardness of water.
Reason (R) : EDTA is a bidentate ligand.
(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is true, but Reason (R) is false.
(d) Assertion (A) is false, but Reason (R) is true.
(2023)

CBSE Sample Questions

5.1 Werner's Theory of Coordination Compounds

MCQ

1. The number of ions formed on dissolving one molecule of $FeSO_4.(NH_4)_2SO_4.6H_2O$ in water is
(a) 3 (b) 4
(c) 5 (d) 6 *(2022-23)*

5.2 Definition of Some Important Terms Pertaining to Coordination Compounds

MCQ

2. Ambidentate ligands like NO_2^- and SCN^- are
(a) unidentate
(b) didentate
(c) polydentate
(d) has variable denticity. *(2020-21)* R

5.3 Nomenclature of Coordination Compounds

MCQ

3. The formula of the coordination compound tetraammineaquachloridocobalt(III) chloride is
(a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(b) $[Co(NH_3)_4(H_2O)Cl]Cl_3$
(c) $[Co(NH_3)_2(H_2O)Cl]Cl_2$
(d) $[Co(NH_3)_4(H_2O)Cl]Cl$ *(2020-21)*

5.4 Isomerism in Coordination Compounds

SA I (2 marks)

4. The formula $Co(NH_3)_5CO_3Cl$ could represent a carbonate or a chloride. Write the structures and names of possible isomers. *(2022-23)*

5.5 Bonding in Coordination Compounds

MCQ

5. The CFSE of $[CoCl_6]^{3-}$ is 18000 cm^{-1}, the CFSE for $[CoCl_4]^-$ will be
   (a) 18000 cm^{-1} (b) 8000 cm^{-1}
   (c) 2000 cm^{-1} (d) 16000 cm^{-1}
   (2022-23)

SA I (2 marks)

6. (i) Using Crystal Field Theory, write the electronic configuration of iron ion in the following complex ion. Also predict its magnetic behaviour : $[Fe(H_2O)_6]^{2+}$
   (ii) Write the IUPAC name of the coordination complex : $[CoCl_2(en)_2]NO_3$

   OR

   (i) Predict the geometry of $[Ni(CN)_4]^{2-}$.
   (ii) Calculate the spin only magnetic moment of $[Cu(NH_3)_4]^{2+}$ ion. *(2020-21)*

SA II (3 marks)

7. Using Valence bond theory, explain the following in relation to the paramagnetic complex $[Mn(CN)_6]^{3-}$
   (a) type of hybridisation
   (b) magnetic moment value
   (c) type of complex – inner, outer orbital complex
   (2022-23)

8. Answer the following questions :
   (a) $[Ni(H_2O)_6]^{2+}_{(aq)}$ is green in colour whereas $[Ni(H_2O)_4(en)]^{2+}_{(aq)}$ is blue in colour, give reason in support of your answer.
   (b) Write the formula and hybridisation of the following compound :
   tris(ethane-1,2–diamine)cobalt(III) sulphate U

   OR

   In a coordination entity, the electronic configuration of the central metal ion is $t_{2g}^3 e_g^1$.
   (a) Is the coordination compound a high spin or low spin complex?
   (b) Draw the crystal field splitting diagram for the above complex. *(Term II, 2021-22)*

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. (c): $[Co(NH_3)_5SO_4]Cl \xrightarrow{AgNO_3} \underset{\text{(white ppt)}}{AgCl\downarrow}$

Only Cl^- ion gets ionise, SO_4^{2-} will not ionise since it is present inside coordination sphere.

2. (a): For one mole of the compound, two moles of AgCl are precipitated which indicates two ionisable chloride ions in the complex. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

3. For one mole of the compound, two moles of AgCl are precipitated which indicates two ionisable chloride ions in the complex. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

Commonly Made Mistake

- Student must know the difference between primary and secondary valency.
- Primary valency - Normally ionisable and are satisfied by negative ions.
- Secondary valency - Non-ionisable and are satisfied by neutral molecules or negative ions.

4. Double salts dissociate into ions completely when dissolved in water. On the other hand, in complexes, the complex ion does not dissociate.

5. Structural formula : $[Co(NH_3)_6]Cl_3$

6. (b): $[Co(en)_3]_2(SO_4)_3$
Let oxidation number of Co be *x*.
$2(+x + 3(0)) = +6$
$2x = +6$
$x = +3$

7. (c): $C_2O_4^{2-}$ is a chelating ligand, it forms a chelate complex with metal ion.

8. (a): The coordination number of Cr in $[CrCl_2(ox)_2]^{3-}$ is 6 as Cl is monodentate ligand and oxalate is bidentate ligand.

9. (b): Ethane-1, 2-diamine (*en*) is a bidentate ligand.

Key Points

- The secondary valency is equal to the coordination number.

10. (d): Formation of chelate rings increases the stability of the complex.

11. (a): As CO is a neutral ligand, its oxidation state is zero. The oxidation state of Ni in $Ni(CO)_4$ is calculated as follows :
$x + 4(0) = 0, x = 0$

12. $[Fe(C_2O_4)_3]^{3-}$ is more stable than $[Fe(NH_3)_6]^{3+}$ due to chelate effect, as it forms rings.

13. Coordination number and oxidation state of Pt in the complex $[Pt(en)_2Cl_2]$ are 6 and +2 because *en* is a bidentate and neutral ligand.

14. $[Co(en)_3]^{3+}$ is more stable complex than $[Co(NH_3)_6]^{3+}$ due to chelate effect as it forms rings.

15. (c): $[Co(NH_3)_4Cl(NO_2)]Cl$
Tetraamminechloridonitrito-N-cobalt(III) chloride

16. $Fe_4[Fe(CN)_6]_3$

17. IUPAC name of the complex $[Cr(NH_3)_3Cl_3]$ is triamminetrichloridochromium(III).

18. Pentaamminecarbonatocobalt(III) chloride

19. IUPAC name of the complex
For one mole of the compound, two moles of AgCl are precipitated which indicates two ionisable chloride ions in the complex. Hence, its structural formula is

$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ is :
Pentaaquachloridochromium(III) chloride.

20. (a) $K_2[Zn(OH)_4]$
Potassium tetrahydroxidozincate(II)
(b) $[Pt(NH_3)_6]Cl_4$
Hexaammineplatinum(IV) chloride

Key Points

- If the complex provides anionic complex ion then the name of the metal ends with the suffix *ate*.

21. (i) $[Co(NH_3)_5(ONO)]Cl_2$ (ii) $K_2[Ni(CN)_4]$

22. (a) $Na[Au(CN)_2]$
Sodium dicyanidoaurate(I)
(b) $[Pt(NH_3)_4(Cl)(NO_2)]SO_4$
Tetraamminechloridonitrito-N-platinum(IV) sulphate

23. (a) $[Cr(en)_3]Cl_3$
Tris(ethane-1,2-diamine)chromium(III) chloride
(b) $K_2[Zn(OH)_4]$
Potassium tetrahydroxidozincate(II)

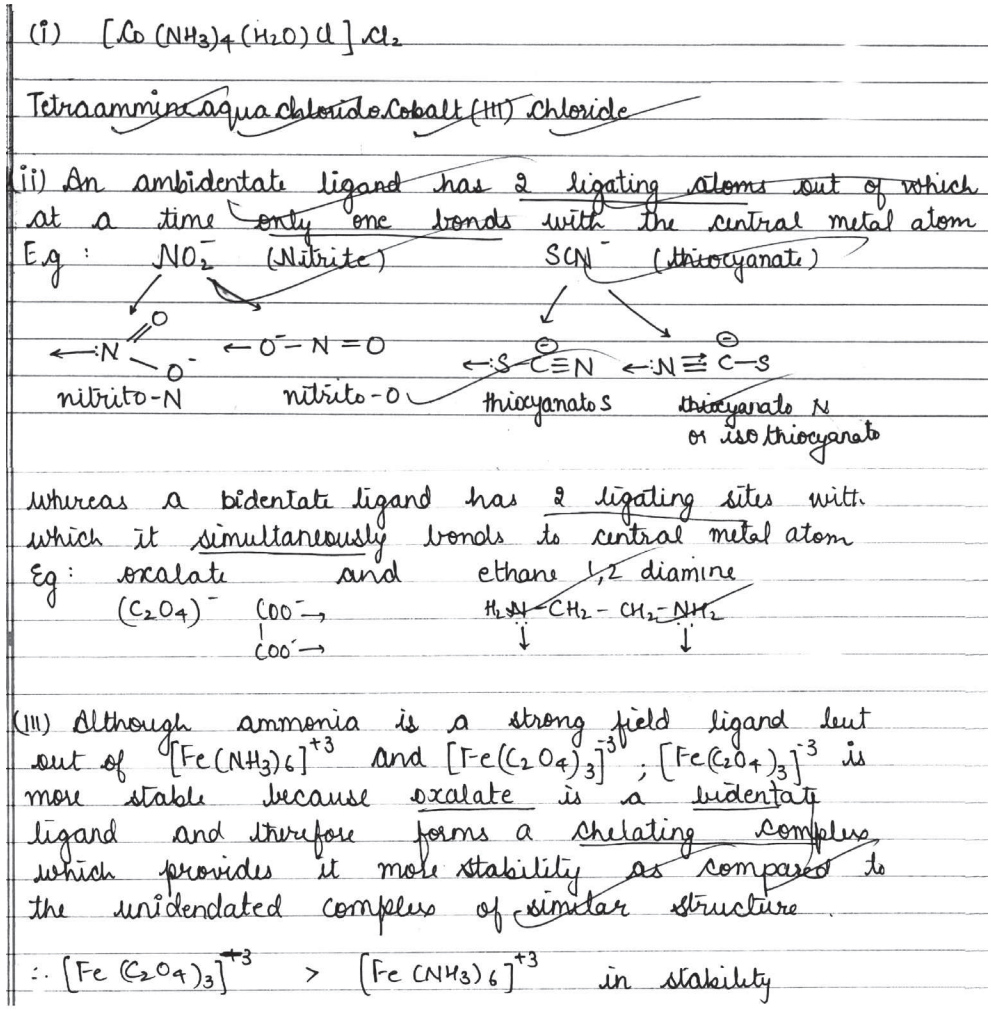
24. (a) $K_3[Al(C_2O_4)_3]$
Potassium trioxalatoaluminate(III)
(b) $[CoCl_2(en)_2]^+$
Dichlorido*bis*(ethane–1,2-diamine)cobalt(III) ion

25. (i) Diamminedichlorido(ethane-1,2-diamine) chromium(III) chloride.
(ii) $[Co(NH_3)_5(ONO)]^{2+}$

26. (i) $[Co(NH_3)_6]Cl_3$
(ii) $K_2[NiCl_4]$

27. (i) *Tris*(ethylenediammine)chromium(III) chloride
(ii) $K_3[Cr(ox)_3]$

28.

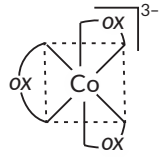

(i) [Co(NH3)4(H2O)Cl]Cl2
Tetraammineaquachloridocobalt(III) chloride
(ii) An ambidentate ligand has 2 ligating atoms out of which at a time only one bonds with the central metal atom
Eg : NO2- (Nitrite) SCN- (thiocyanate)
nitrito-N
nitrito-O
thiocyanato S
thiocyanato N or isothiocyanato
whereas a bidentate ligand has 2 ligating sites with which it simultaneously bonds to central metal atom
Eg : oxalate and ethane 1,2 diamine
(C2O4)2-
H2N-CH2-CH2-NH2
(iii) Although ammonia is a strong field ligand but out of [Fe(NH3)6]+3 and [Fe(C2O4)3]-3 ; [Fe(C2O4)3]-3 is more stable because oxalate is a bidentate ligand and therefore forms a chelating complex which provides it more stability as compared to the unidendated complex of similar structure.
∴ [Fe(C2O4)3]+3 > [Fe(NH3)6]+3 in stability

[Topper's Answer, 2022]

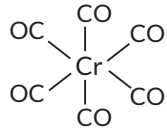
29. (i) Hexaamminecobalt(III) chloride
(ii) Tetrachloridonickelate(II) ion
(iii) Potassium hexacyanidoferrate(III)

30. (i) Pentaamminechloridocobalt(III) chloride
(ii) Potassium hexacyanidoferrate(III)
(iii) Tetrachloridonickelate(II) ion

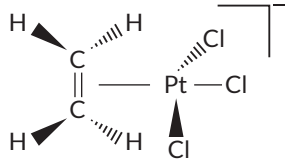
31. (i) Trioxalatocobaltate(III)



(ii) Hexacarbonylchromium(0)



(iii) Trichloridoetheneplatinate(II) ion



32. **(c) :** Compounds, which give different ions in solution due to the exchange of ions in coordination sphere and counter ions are called ionisation isomers.
Therefore, $[Co(Br)(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5]Br$ are ionisation isomers.

33. **(c) :** The pair $[Co(NH_3)_4Cl_2]Br_2$ and $[Co(NH_3)_4Br_2]Cl_2$ will show ionisation isomerism.

34. **(a)**

35. Linkage isomerism is shown by the given complex as NO_2 is an ambidentate ligand. The resultant linkage isomers are $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$.
Ionisation isomerism is also shown by the given complex as $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5Cl]NO_2Cl$

36. Ionisation isomerism : $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$

37. Coordination isomerism

38. The complex $[Co(NH_3)_5(SCN)]^{2+}$ shows linkage isomerism as SCN^- is an ambidentate ligand.

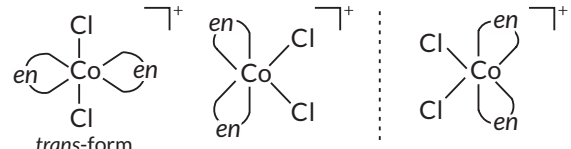
39. Linkage isomerism : $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(ONO)(NH_3)_5]^{2+}$

Concept Applied

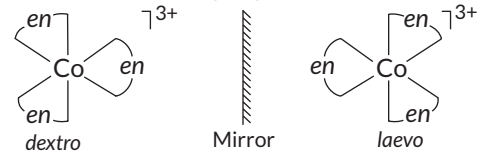
➲ Linkage isomerism arises in a coordination compound containing ambidentate ligand.

40. (a) An atom, molecule or ion which is linked to central metal atom or ion through coordinate bond by donating lone pair of electrons present on its donor atom is known as ligand.
Here, NH_4^+ cannot act as a ligand since there is no lone pair of electrons on its donor atom.
(b) Linkage isomer of $[Co(NH_3)_5(NO_2)]Cl_2$ is $[Co(NH_3)_5(ONO)]Cl_2$
IUPAC name : Pentaamminenitrito-O-cobalt(III) chloride.

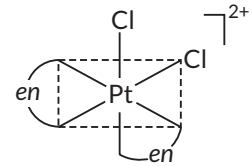
41. $[CoCl_2(en)_2]^+$: Dichlorido*bis*(ethane-1,2-diamine) cobalt(III) ion
This complex exhibit both optical and geometrical isomerism and *cis* isomer is optically active.



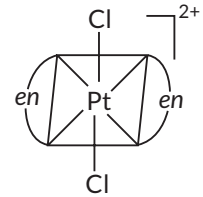
42. The complex, $[Co(en)_3]Cl_3$ shows optical isomerism.



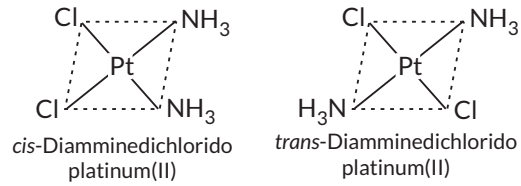
43. *Cis*-isomer of the complex $[Pt(en)_2Cl_2]^{2+}$ is optically active.



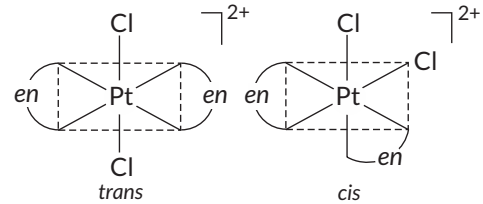
44. *Trans*-isomer is optically inactive due to the presence of plane of symmetry.



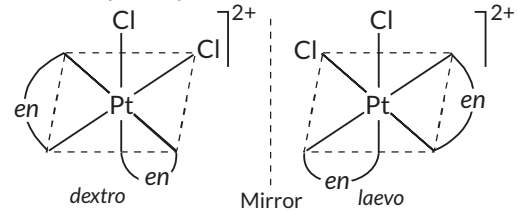
45. Geometrical isomers



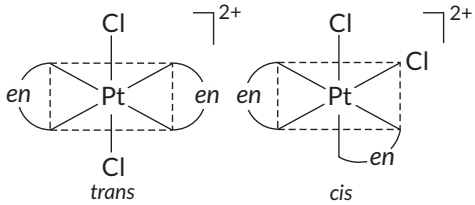
46. IUPAC name - Dichlorido*bis*(ethane-1,2-diamine) platinum(IV) ion. This complex shows geometrical and optical isomerism.



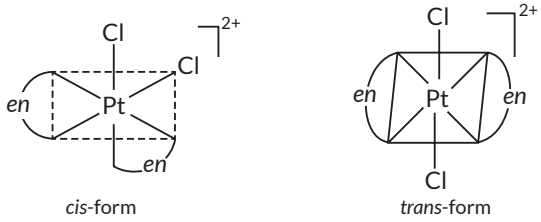
Cis-isomer is optically active.



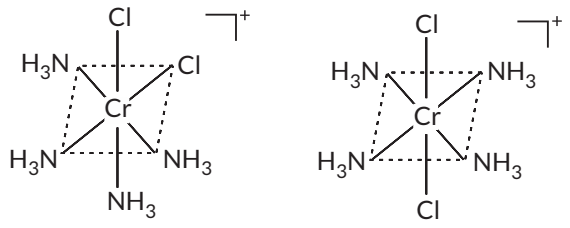
47. This complex shows geometrical and optical isomerism. Geometrical isomers are *cis-trans* isomers.



48. $[Pt(en)_2Cl_2]$
Dichloridodiethylenediamine platinum(II)
Geometrical isomers of $[Pt(en)_2Cl_2]$ are

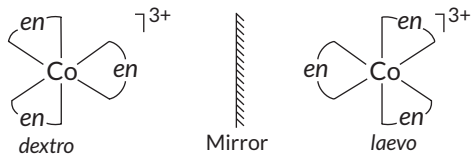


49. Tetraamminedichloridochromium(III) ion
Geometrical isomers of $[Cr(NH_3)_4Cl_2]^+$;

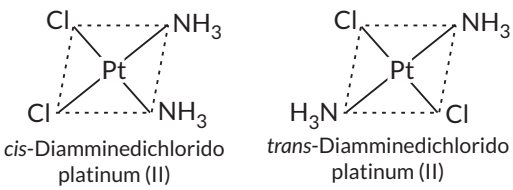


50. (i) Linkage isomerism : $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$

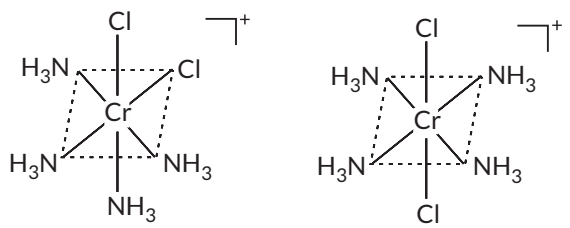
(ii) Optical isomerism : $[Co(en)_3]Cl_3$



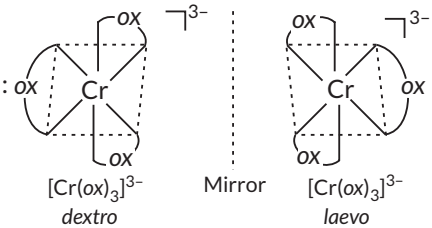
(iii) Geometrical isomerism : $[Pt(NH_3)_2Cl_2]$



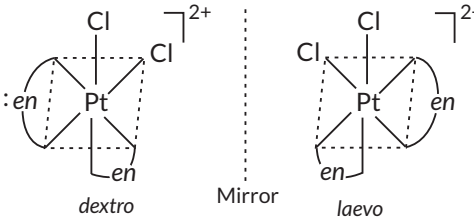
51. Tetraamminedichloridochromium(III) ion $[Cr(NH_3)_4Cl_2]^+$ shows geometrical isomerism.



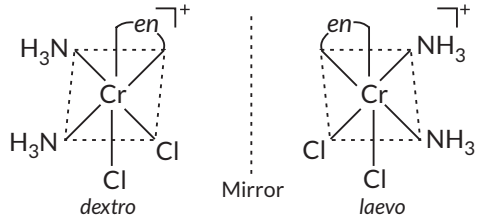
52. $[Cr(C_2O_4)]^{3-}$:



$[PtCl_2(en)_2]^{2+}$:



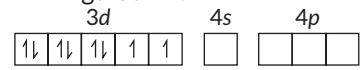
$[Cr(NH_3)_2Cl_2(en)]^+$:



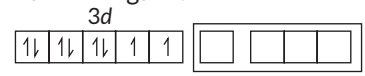
Key Points

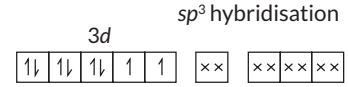
- Optical isomers are mirror images that cannot be superimposed on one another.

53. **(b):** In $[NiCl_4]^{2-}$, Ni is in +2 oxidation state and has $3d^8$ outer electronic configuration .

Orbital of Ni^{2+} ion 

Since, Cl^- is a weak field ligand.

sp^3 hybridised orbital of Ni^{2+} 

$[NiCl_4]^{2-}$ 

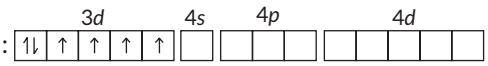
high spin complex

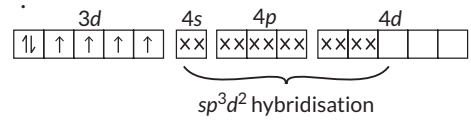
It is sp^3 hybridised high spin paramagnetic complex.

$\mu = \sqrt{n(n+2)}$

$= \sqrt{2(2+2)} = \sqrt{2\times 4} = \sqrt{8} = 2{\cdot}82$ B.M.

54. The IUPAC name of $[CoF_6]^{3-}$ is hexafluoridocobaltate(III).
Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.

Co^{3+} : 

Co^{3+} in $[CoF_6]^{3-}$: 

No. of unpaired electrons = 4

Key Points

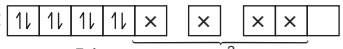
- Weak field ligands give, outer orbital or high spin or spin free complex.

55. $[Pt(CN)_4]^{2-}$ has square planar structure.

Pt : [Xe] $4f^{14}\ 5d^9\ 6s^1$

Pt^{2+} : [Xe] $4f^{14}\ 5d^8\ 6s^0$

$[Pt(CN)_4]^{2-}$:



No. of unpaired electrons = 0.

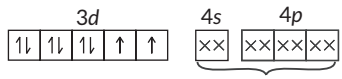
56. The complex $[Co(C_2O_4)_3]^{3-}$ has d^2sp^3-hybridisation and it is diamagnetic in nature due to the absence of unpaired electrons.

57. $[NiCl_4]^{2-}$ contains Ni^{2+} ion with $3d^8$ configuration.

Ni^{2+} : Ground state

Cl^- is a weak field ligand thus no pairing will occur. Hence, outer 4*s* and 4*p*-orbitals are used in hybridisation.

$[NiCl_4]^{2-}$: with 4Cl^- ligands

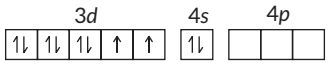


sp^3 hybridisation, (tetrahedral)
4 electron pairs donated by 4Cl^- ligands (weak field ligand)

It has two unpaired electrons hence, it is paramagnetic.

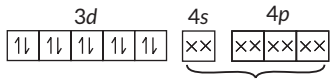
$[Ni(CO)_4]$ contains Ni(0) – $3d^84s^2$ configuration.

Ni(0) : Ground state



CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.

$[Ni(CO)_4]$:



sp^3 hybridisation (tetrahedral) four electrons donated by four CO ligands (strong field ligand)

The complex has all paired electrons hence, it is diamagnetic.

Key Points

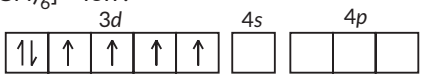
- Strong field ligands give, inner orbital or low spin or spin paired complex. Weak field ligands give, outer orbital or high spin or spin free complex.

58. (i) $[Mn(H_2O)_6]SO_4$

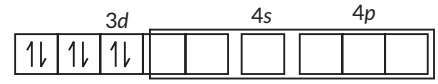
Hexaaquamanganese(II) sulphate

(ii) $[Fe(CN)_6]^{4-}$ ion :

Fe^{2+} ion :

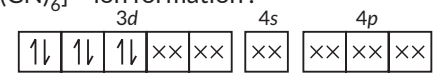


Fe^{2+} ion hybridised (under the influence of strong field ligand).



Six empty d^2sp^3 hybrid orbitals

$[Fe(CN)_6]^{4-}$ ion formation :



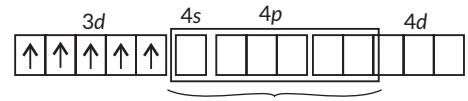
Six pairs of electrons from six CN^- ions (d^2sp^3)

Since, the complex ion does not contain any unpaired electron, so it is diamagnetic.

$[FeF_6]^{3-}$ ion :

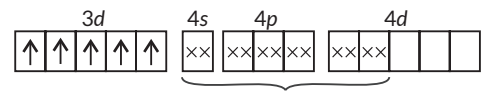
Fe^{3+} ion :

Fe^{3+} ion hybridised (under the influence of weak field ligand).



Six empty sp^3d^2 hybrid orbitals

$[FeF_6]^{3-}$ ion formation :



Six electrons pairs from six F^- ions (sp^3d^2)

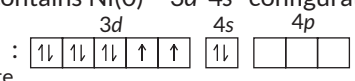
As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9$ B.M.

59. (i) IUPAC name; Tetracarbonylnickel(0)

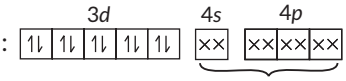
$[Ni(CO)_4]$ contains Ni(0) – $3d^84s^2$ configuration.

Ni(0) : Ground state



CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.

$[Ni(CO)_4]$:

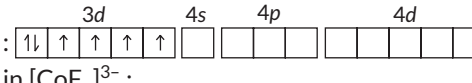


sp^3 hybridisation (tetrahedral) four electrons donated by four CO ligands (strong field ligand)

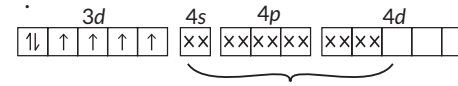
(ii) The IUPAC name of $[CoF_6]^{3-}$ is hexafluoridocobaltate(III).

Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.

Co^{3+} :



Co^{3+} in $[CoF_6]^{3-}$:



sp^3d^2 hybridisation six pairs of electrons from six F^- ion (Weak field ligands)

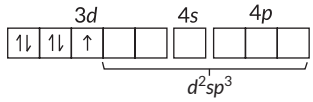
60. (a) $[Fe(CN)_6]^{3-}$

IUPAC name : Hexacyanidoferrate (III) ion

Fe is present as Fe^{3+} in $[Fe(CN)_6]^{3-}$

Fe^{3+} : [Ar] $3d^5\ 4s^0$

As CN^- is a strong field ligand, hence, electrons in 3*d* get paired up.

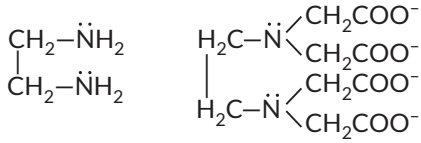


Hybridisation is d^2sp^3.

(b) Ambidentate ligands : These are the unidentate ligands containing more than one coordinating atoms are called ambidentate ligands.

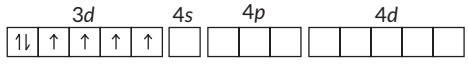
For example NO_2; it can donate through –N or –O both.

Chelating ligands : Bidentate or polydentate ligands which contain two or more donor atoms and these are positioned in such a way that a five or six membered ring is formed with metal ion. for example ethylenediamine and $EDTA^-$.



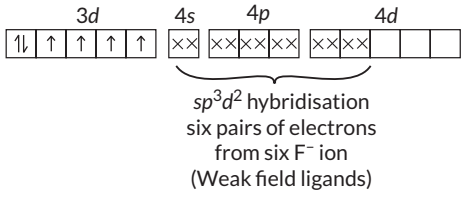
61. Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.

Co^{3+} :

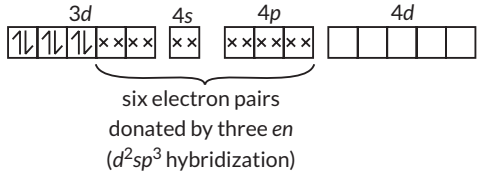


(In ground state)

$[CoF_6]^{3-}$:



$[Co(en)_3]^{3+}$:



(i) $[CoF_6]^{3-}$ is paramagnetic in nature.

(ii) Chelating ligands form more stable cyclic/ring complexes than unidentate or non-chelating ligands. Since, $[Co(en)_3]^{3+}$ contains *en* which is a bidentate chelating ligand, it is more stable than $[CoF_6]^{3-}$.

(iii) $[Co(en)_3]^{3+}$ is an inner orbital complex as its hybridisation is d^2sp^3 hybridisation.

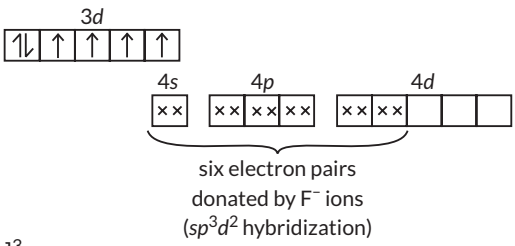
(iv) $[CoF_6]^{3-}$ is a high spin complex.

Concept Applied

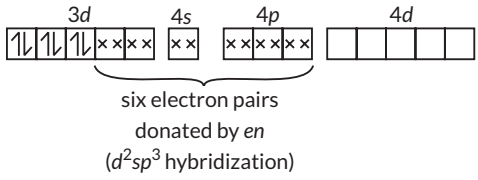
➲ Strong field ligand forms low spin, inner orbital complexes and weak field ligands from high spin outer orbital complex.

62. Formation of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ can be represented as :

$[CoF_6]^{3-}$:



$[Co(C_2O_4)_3]^{3-}$:



(i) $[Co(C_2O_4)_3]^{3-}$ is diamagnetic as all electrons are paired.

(ii) $[Co(C_2O_4)_3]^{3-}$ is more stable as $C_2O_4^{2-}$ is a chelating ligand and forms chelate rings.

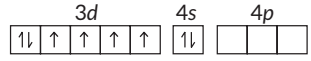
(iii) $[CoF_6]^{3-}$ is outer orbital complex as it undergoes sp^3d^2 hybridization using the outer 4*d*-orbital.

(iv) $[Co(C_2O_4)_3]^{3-}$ is low spin complex due to absence of any unpaired electron.

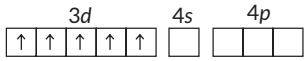
63. $[Fe(H_2O)_6]^{3+}$:

Fe atom (*Z* = 26)

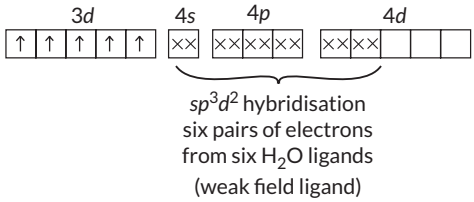
Ground state :



Fe^{3+} ion :



$[Fe(H_2O)_6]^{3+}$:

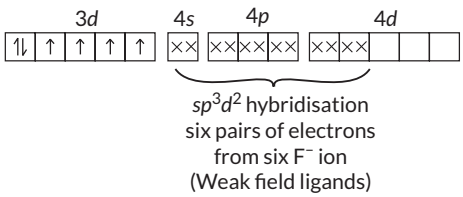


The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of five unpaired electrons.

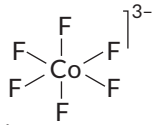
64. (i) Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.

Co^{3+} :

$[CoF_6]^{3-}$:

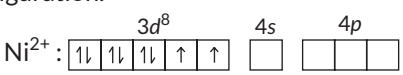


Structure – Outer orbital octahedral complex



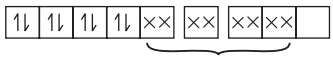
Nature – Paramagnetic

(ii) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration.



(In ground state)

$[Ni(CN)_4]^{2-}$:

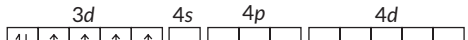


dsp^2 hybridisation
four electrons pairs
donated by four
CN^- ions
(Strong field ligand)

The complex ion has square planar geometry and is diamagnetic in nature.

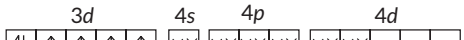
65. Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.

Co^{3+} :



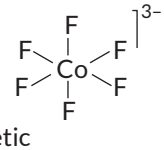
(In ground state)

$[CoF_6]^{3-}$:



sp^3d^2 hybridisation
six pairs of electrons
from six F^- ion
(Weak field ligands)

Structure – Outer orbital octahedral complex



Nature – Paramagnetic
IUPAC Name : Hexafluoridocobaltate(III) ion

Key Points

- F^- is a weak field ligands.

66. In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration.

Ni^{2+} :

$[Ni(CN)_4]^{2-}$:

dsp^2 hybridisation
four electrons pairs
donated by four
CN^- ions
(Strong field ligand)

The complex ion has square planar geometry and is diamagnetic in nature.
IUPAC name : Tetracyanidonickelate(II) ion

67. Oxidation of cobalt in $[Co(NH_3)_6]^{3+}$ is +3.

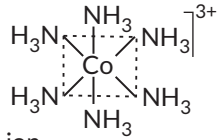
Co^{3+} :

Ground State

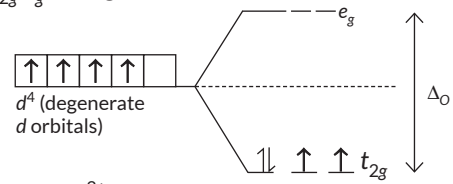
$[Co(NH_3)_6]^{3+}$ ion :

d^2sp^3 hybridisation
six pairs of electrons
from six NH_3 ligand
(Strong field ligand)

Hybridisation – d^2sp^3
Structure – Octahedral
(low spin)
Nature – Diamagnetic
IUPAC name : Hexaamminecobalt(III) ion



68. (a) On the basis of CFT, if strong field ligand is present for d^4 orbit with $\Delta_o > P$, the energy gap between t_{2g} and e_g will be more and thus the electron will pair up giving $t_{2g}^4 e_g^0$ configuration.

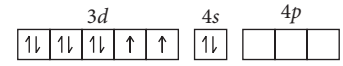


(b) $[Ni(H_2O)_6]^{2+}$ is a high spin complex (Δ_o small).

In $[Ni(H_2O)_6]^{2+}$, d-d transitions are taking place on absorbing low energy radiation (red component of spectrum) from visible region showing green as the complementary colour.

$[Ni(CO)_4]$ contains Ni(0) – $3d^8 4s^2$ configuration.

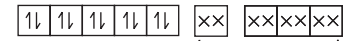
Ni(0) :



Ground state

CO is a strong field ligand hence, 4s-electrons will shift to 3d-orbital making 4s-orbital vacant.

$[Ni(CO)_4]$:



sp^3 hybridisation
(tetrahedral)
four electrons
denoted by four
CO ligands
(strong ligand)

The complex has all paired electrons hence, it is colourless.

69. (a) Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3.

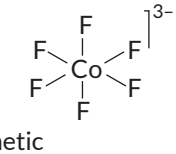
Co^{3+} :

(In ground state)

$[CoF_6]^{3-}$:

sp^3d^2 hybridisation
six pairs of electrons
from six F^- ion
(Weak field ligands)

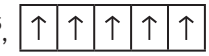
Structure – Outer orbital octahedral complex



Nature – Paramagnetic
(b) $[Co(NH_3)_5Cl]Cl$
Pentaamminechloridocobalt(III) chloride

70. (i) $[FeF_6]^{3-}$
Oxidation state of Fe = +3

Fe^{3+} : $3d^5$,



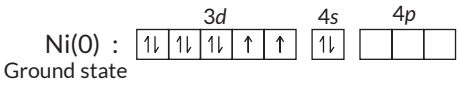
3d-orbitals

$\mu_{spin} = \sqrt{n(n+2)}$ B.M. $= \sqrt{5(5+2)}$ B.M $= 5.91$ B.M.

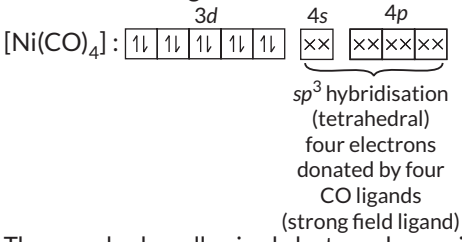
(ii) Pentaamminechloridocobalt(III) chloride
(iii) Chelating ligands form more stable cyclic/ring complexes than unidentate or non-chelating ligands.

Since, $[Co(en)_3]^{3+}$ contains *en* which is a bidentate chelating ligand, it is more stable than $[CoF_6]^{3-}$.

71. (a) $[Ni(CO)_4]$ contains Ni(0) – $3d^8 4s^2$ configuration.



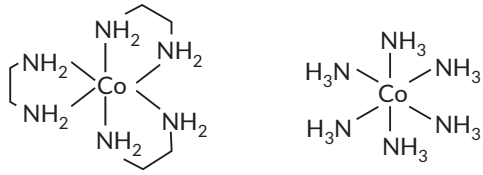
CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.



The complex has all paired electrons hence, it is diamagnetic.

(b) Diamminechloridonitrito-N-platinum(II)

(c) $[Co(en)_3]^{3+}$ is a complex having bidentate ligand (*en*) that form a five - membered ring around Co metal that results in chelation. While no such ring is formed in $[Co(NH_3)_6]^{3+}$ complex. So, $[Co(en)_3]^{3+}$ is more stable due to chelation.



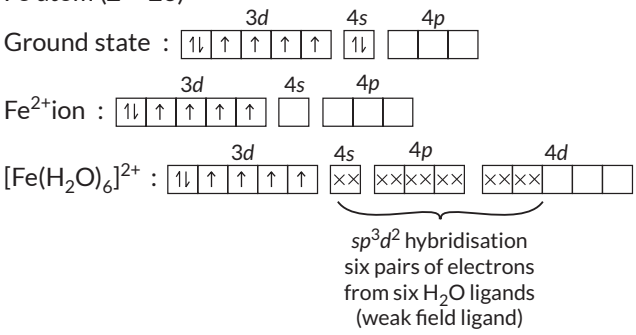
(*en* = ethylenediamine)

Key Points

- Chelating ligands form more stable complexes.

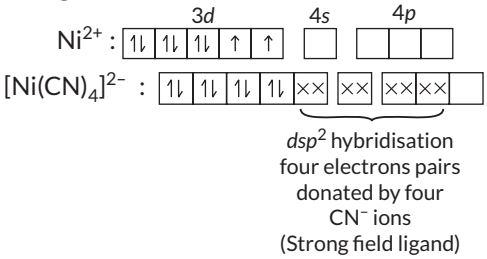
72. (i) $[Fe(H_2O)_6]^{2+}$:

Fe atom ($Z = 26$)



The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of four unpaired electrons.

(ii) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration.



The complex ion has square planar geometry and is diamagnetic in nature.

73. (i) Its formula will be $[Pt(NH_3)_2Cl_2]$.

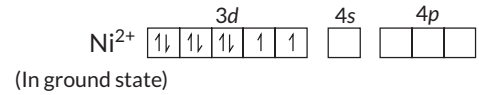
(ii) *en* is a bidentate ligand. Hence in $[Co(en)_3]^{3+}$, its secondary valency is 6.

(iii) (1) $Fe_4[Fe(CN)_6]_3$ is Iron (III) hexacyanidoferrate(II).

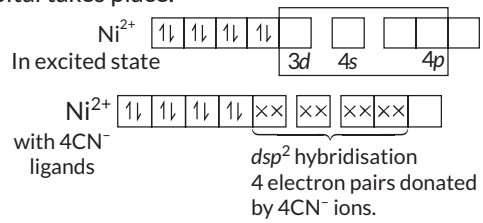
(2) IUPAC name of $[Co(NH_3)_5Cl]Cl_2$ is pentaammine chloridocobalt(III) chloride.

OR

(iii) In $[Ni(CN)_4]^{2-}$, Ni is present as Ni(II) with $3d^8$-configuration.



CN^- is a strong field ligand. Hence pairing of electrons in 3*d*-orbital takes place.



It has all paired electrons, hence it is diamagnetic.

74. (a): If $\Delta_o < P$ (*i.e.*, Δ_o small, weak field ligand) $\rightarrow$ electrons spread out among all *d*-orbitals before pairing up $\rightarrow$ forms high spin complex.

For tetrahedral crystal field, the order of splitting is reversed and is related to Δ_o as

$$\Delta_t = \frac{4}{9}\Delta_o$$

Consequently the orbital splitting energies are not sufficiently large for forcing pairing and therefore, low spin configurations are rarely observed in tetrahedral coordination entities.

75. (c)

76. $[Ni(H_2O)_6]^{2+}$ is a high spin complex (Δ_o small) while $[Ni(CN)_4]^{2-}$ is a low spin square planar complex.

In $[Ni(H_2O)_6]^{2+}$ complex, *d-d* transitions are taking place on absorbing low energy radiation (red component of spectrum) from visible region showing green as the complementary colour.

In $[Ni(CN)_4]^{2-}$ complex, *d-d* transitions do not take place because there is no unpaired electron present hence, complex is colourless.

77. (a) Due to the presence of weak field ligand, *i.e.*, Cl^- in the complex $[NiCl_4]^{2-}$ two unpaired electrons are present in 3*d*-orbitals of Ni-atom hence, this complex is paramagnetic in nature. On the other hand, due to the presence of strong field ligand *i.e.*, CN^- in the complex $[Ni(CN)_4]^{2-}$, no unpaired electron is present in 3*d*-orbitals of Ni-atom (as strong field ligand causes pairing of electrons), hence, it is diamagnetic in nature.

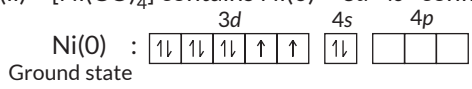
(b) In tetrahedral coordination entity formation, the *d*-orbital splitting is smaller. Consequently, the orbital splitting energies are not sufficiently large to force

pairing and therefore, low spin configurations are rarely observed.

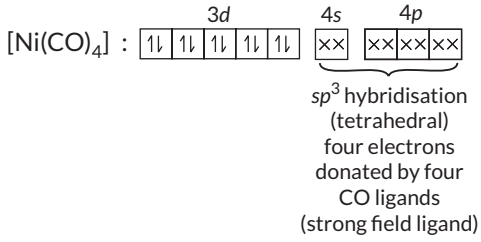
78. (i) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.

Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

(ii) $[Ni(CO)_4]$ contains Ni(0) – $3d^8 4s^2$ configuration.



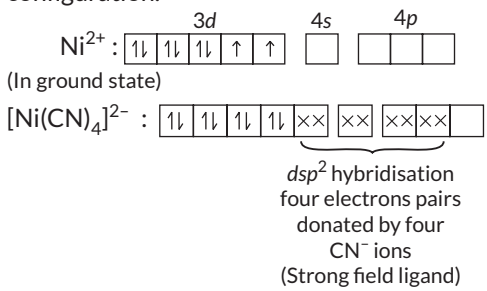
CO is a strong field ligand hence, 4*s*-electrons will shift to 3*d*-orbital making 4*s*-orbital vacant.



The complex has all paired electrons hence, it is diamagnetic.

79. (i) When $\Delta_o < P$, $t_{2g}^3 e_g^1$

(ii) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration.



The complex ion has square planar geometry and is diamagnetic in nature.

(iii) $[Co(en)_2Cl_2]^+$

Dichlorido*bis*(ethane-1,2-diamine)cobalt(III) ion

80. (i) For d^4 ion, if $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.

Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

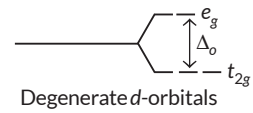
(ii) Due to the presence of weak field ligand, *i.e.*, Cl^- in the complex $[NiCl_4]^{2-}$ two unpaired electrons are present in 3*d*-orbitals of Ni-atom hence, this complex is paramagnetic in nature. On the other hand, due to the presence of strong field ligand *i.e.*, CN^- in the complex $[Ni(CN)_4]^{2-}$, no unpaired electron is present in 3*d*-orbitals of Ni-atom (as strong field ligand causes pairing of electrons), hence, it is diamagnetic in nature.

(iii) $[PtCl_2(NH_3)_4]Cl_2 \rightarrow [PtCl_2(NH_3)_4]^{2+}_{(aq)} + 2Cl^-_{(aq)}$

Hence, the total number of ions produced is three.

81. (a) $K_3[Cr(C_2O_4)_3]$: Potassium trioxalatochromate(III)

(b) According to crystal field theory, five *d*-orbitals, split into two different energy levels termed as t_{2g} and e_g as shown below :



For d^5 ion with $\Delta_o < P$, electronic configuration will be $t_{2g}^3 e_g^2$.

Concept Applied

➲ Weak field ligands causes less splitting, for these $\Delta_o < P$, hence before pairing electron goes to higher e_g level, causing formation of high spin complexes.

(c) Ambidentate ligand : A unidentate ligand which can coordinate to central metal atom through two different atoms is called ambidentate ligand. For example, NO_2^- ion can coordinate either through nitrogen or through oxygen to the central metal atom/ion.

82. (i) $K_2[PdCl_4]$: Potassium tetrachloridopalladate(II)

(ii) If $\Delta_o > P$, it becomes energetically favourable for the fourth and fifth electron to occupy in t_{2g} orbital with the resultant configuration $t_{2g}^5 e_g^0$. Such an effect is produced by strong field ligand and such a complex formed is referred to as low spin complex.

(iii) Homoleptic complexes : Complexes in which a metal is bond to only one kind of ligand are called homoleptic complexes.

e.g., $[Co(NH_3)_6]^{3+}$, $[Cu(CN)_6]^{3-}$, $[Ti(H_2O)_6]^{3+}$

83. (i) The complexes formed by chelating ligand are more stable than that formed by unidentate ligand because of multiple points of attachment of the ligand with the central atom/ion and formation of stable cyclic closed ring structures.

(ii) A spectrochemical series is an experimentally determined series based on the absorption of light by complexes with different ligands. It contains an arrangement of ligands in increasing order of their field strength. The series can be listed as :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

A strong field ligand produces a stronger field and causes greater splitting of the *d*-orbitals. In this case, pairing of electrons occurs. For example : CO, CN^-, etc. On the other hand, a weak field ligand produces a weak field and causes lesser splitting of *d*-orbitals. In such case, pairing of electrons does not occur. For example : Cl^-, Br^-, I^-, etc.

84. (a) $K_4[Mn(CN)_6]$

Potassium Hexacyanomanganate(II)

In $K_4[Mn(CN)_6]$, Mn is present in +2 oxidation state.

Mn^{2+} : d^5 configuration

In presence of strong ligand, $\Delta_o < P$

Hence : $t_{2g}^5 e_g^0$

(b) A ligand which forms two or more bonds with central atom or ion and results in the formation of stable cyclic complex is called chelating ligand and the effect is called chelating effect. For example, oxalate, ethylene diamine, dimethyl glyoxime, etc.

85. (a) Ambidentate ligand : Ligands having two different atoms through which it can act as a ligand

For example,

CN^- CN^- : $\overset{\text{Cyanido-C}}{\leftarrow\!\!-C\equiv N}$ or $\overset{\text{Cyanido-N}}{\ddot{C}=\ddot{N}:\rightarrow}$

(b) A spectrochemical series is an experimentally determined series based on the absorption of light by complexes with different ligands. It contains an arrangement of ligands in increasing order of their field strength. The series can be listed as :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

(c) Heteroleptic complexes : Complexes in which the central atom is bound to different type of ligands are called *heteroleptic complexes*.

e.g., $[Co(NH_3)_4Cl_2]$, $K_2[Fe(CN)_5NO]$, $[Fe(H_2O)_5NO]SO_4$

86. In CO, both lone pair of electrons and vacant π^* orbitals are present. Hence, it acts as electron pair σ donor as well as π acceptor by back bonding. Hence, *M*—CO bond is stronger.

$$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} CO$$

NH_3 is electron pair donor only. Accumulation of negative charge on the metal ion takes place, hence *M*—NH_3 bond is weaker.

$M \leftarrow NH_3$

87. (c) : Hardness of water is estimated by titration with EDTA. EDTA is a hexadentate ligand.

CBSE Sample Questions

1. (c) : 1 mole of Mohr's salt gives 1 Fe^{2+}, $2SO_4^{2-}$ and $2NH_4^+$ ions on dissolving in water. The total number of ions is 5. **(1)**

2. (a) : Ambidentate ligands such as NO_2^-, SCN^- are unidentate ligands. **(1)**

3. (a) : Tetraammineaquachloridocobalt(III) chloride : $[Co(NH_3)_4(H_2O)Cl]Cl_2$ **(1)**

4. $[Co(NH_3)_5CO_3]Cl$ and $[Co(NH_3)_5Cl]CO_3$

Pentaamminecarbonatocobalt(III) chloride

Pentaamminechloridocobalt(III) carbonate **(2)**

5. (b) : Using equation, $\Delta_t = \frac{4}{9}\Delta_o$

$\Delta_t = (4/9) \times 18000\ cm^{-1} = 8000\ cm^{-1}$ **(1)**

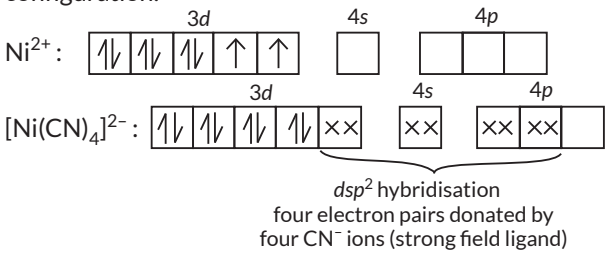
6. (i) Electronic configuration : $t_{2g}^4 e_g^2$ **(1/2)**

This complex is paramagnetic due to the presence of four unpaired electrons. **(1/2)**

(ii) Dichloridobis(ethane-1,2-diamine)cobalt(III) nitrate **(1)**

OR

(i) In $[Ni(CN)_4]^{2-}$: Ni is present as Ni(II) with $3d^8$ configuration.



∴ The complex ion has a square planar geometry. **(1)**

(ii) Cu(*Z* = 29) : [Ar] $3d^{10}4s^1$

Cu^{2+} : $3d^9$

Number of unpaired electron = 1

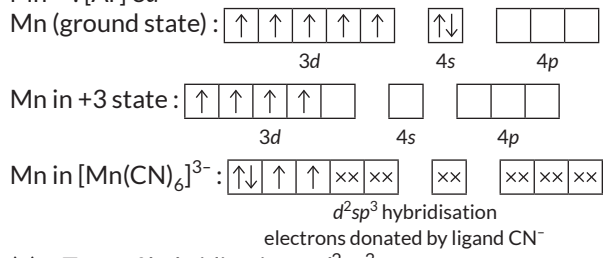
Magnetic moment, $\mu_B = \sqrt{n(n+2)}$

$= \sqrt{1(1+2)} = 1.73$ B.M. **(1)**

7. $[Mn(CN)_6]^{3-}$

Mn : [Ar] $3d^5 4s^2$

Mn^{3+} : [Ar] $3d^4$



(a) Type of hybridisation – d^2sp^3 **(1)**

(b) Magnetic moment value =

$\sqrt{n(n+2)} = \sqrt{(2(2+2))} = 2.83$ B.M.

(*n* = no. of unpaired electrons) **(1)**

(c) Type of complex – inner orbital complex. **(1)**

8. (a) The colour of coordination compounds depends upon the type of ligands and *d-d* transition taking place.

H_2O is weak field ligand, which causes small splitting, leading to the *d-d* transition corresponding green colour, however due to the presence of ethane-1,2-diamine (*en*) which is a strong field ligand, the splitting is increased.

Due to the change in t_{2g} – e_g splitting the colouration of the compound changes from green to blue. **(1)**

(b) Formula of the compound is $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$. **(1)**

The hybridisation of the compound is d^2sp^3.

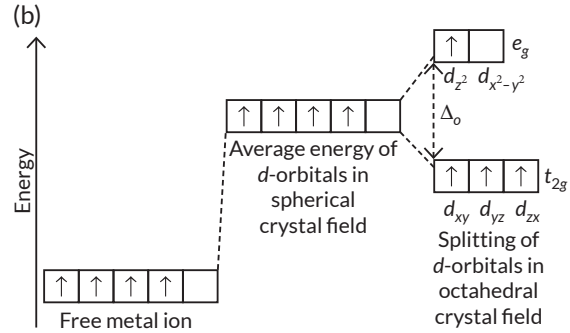
Cobalt in this complex has an oxidation number of +3. The electronic configuration of Co^{3+} : $3d^6\ 4s^0$ and *en* is a strong field ligand that will cause pairing of electrons in *d*-orbital of Co^{3+}.

(1)

OR

(a) As the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\ e_g^1$, *i.e.*, no pairing of electrons which indicates $\Delta_o < P$ hence, it is a high spin complex. **(1)**

(b)



(2)

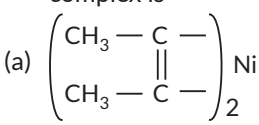
Self Assessment

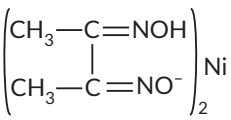
Case Based Questions (5 marks)

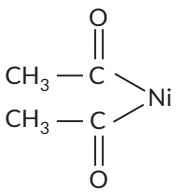
1. Read the passage given below and answer the following questions :

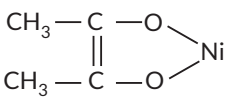
The molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in the solid as well as in the dissolved state are called coordination compounds. Their properties are completely different from the constituents. In coordination compounds, the central metal atom or ion is linked to a number of ions or neutral molecules, called ligands, by coordinate bonds. For example, dimethyl glyoxime (*dmg*) is a bidentate ligand chelate large amounts of metals. When dimethyl glyoxime is added to alcoholic solution of $NiCl_2$ and ammonium hydroxide is slowly added to it, a rosy red precipitate of a complex is formed.

(i) The structure of the rosy red precipitate complex is

(a) 

(b) 

(c) 

(d) 

(ii) Oxidation number of Ni in the given complex is

(a) +3 (b) +1 (c) +2 (d) zero.

(iii) Hybridisation and shape of the complex is

(a) sp^3, tetrahedral

(b) dsp^2, square planar

(c) sp^3, square planar

(d) sp^3d, trigonal bipyramidal.

(iv) Which of the following is true about this complex?

(a) It is paramagnetic, containing two unpaired electrons.

(b) It is paramagnetic, containing one unpaired electron.

(c) It is paramagnetic, containing four unpaired electrons.

(d) It is diamagnetic with no unpaired electron.

(v) Which one will give test for Fe^{3+} ions in the solution?

(a) $[Fe(CN)_6]^{3-}$

(b) $[Fe(CN)_6]^{2-}$

(c) $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$

(d) $Fe_2(SO_4)_3$

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

2. Assertion : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
Reason : Because it has d^2sp^3 type hybridisation.

3. Assertion : Toxic metal ions are removed by the chelating ligands.
Reason : Chelated complexes tend to be more stable.

Multiple Choice Questions (1 mark)

4. Which of the following species is not expected to be a ligand?

(a) NO^+ (b) NH_4^+

(c) $NH_2CH_2CH_2NH_2$ (d) CO

5. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be

(a) 18,000 cm^{-1} (b) 16,000 cm^{-1}

(c) 8,000 cm^{-1} (d) 20,000 cm^{-1}

6. When 1 mol $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained. The formula of the complex is

(a) $[CrCl_3(H_2O)_3] \cdot 3H_2O$

(b) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$

(c) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

(d) $[Cr(H_2O)_6]Cl_3$

7. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are

(a) linkage isomers

(b) coordination isomers

(c) ionisation isomers

(d) geometrical isomers.

VSA Type Questions (1 mark)

8. Indicate primary and secondary valencies of central metal ion in the following complexes.

(a) $[Cr(NH_3)_6]Cl_3$ (b) $K_4[Fe(CN)_6]$

9. Which type of isomerism is shown by $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$?

10. What are strong field ligands? Give an example.

OR

What are metal carbonyls?

SA I Type Questions (2 marks)

11. Explain with examples homoleptic and heteroleptic complexes.
12. For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridization, magnetic character and spin of the complex. (At. number Fe = 26)
13. Write the structures and names of the following complexes and their ionisation isomers.
(a) $[Co(NH_3)_5Br]SO_4$ and
(b) $[Pt(NO_2)(H_2O)(NH_3)_2]Br$.
14. Geometrical isomerism is not found in tetrahedral complexes. Why?
15. Write the formula of the following complexes:
(i) Pentaamminechloridocobalt(III)
(ii) Lithium tetrahydroaluminate(III).
16. Explain the diamagnetic nature of $[Ni(CN)_4]^{2-}$ ion.

OR

Square planar complexes do not show optical isomerism. Why?

SA II Type Questions (3 marks)

17. Why are low spin tetrahedral complexes not formed?
18. Give the electronic configuration of the following complexes on the basis of crystal field splitting theory.
$[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$
19. One mole of $Co(NH_3)_5Cl_3$ gives three moles of ions on dissociation in water. One mole of this reacts with two moles of $AgNO_3$ to give two moles of AgCl. Name the complex.
20. Explain the following :
(i) Anhydrous $CuSO_4$ is white while hydrated $CuSO_4$ is blue in colour.
(ii) $[Ti(H_2O)_6]Cl_3$ is violet in colour but becomes colourless on heating.

OR

$[FeF_6]^{3-}$ has five unpaired electrons while $[Fe(CN)_6]^{3-}$ has only one unpaired electron. Why?

Case Based Questions (4 marks)

21. **Read the passage given below and answer the following questions :**
Coordination compounds are formulated and named according to the IUPAC system.
Few rules for naming coordination compounds are :
– In ionic complex, the cation is named first and then the anion.
– In the coordination entity, the ligands are named first and then the central metal ion.
– When more than one type of ligands are present, they are named in alphabetical order of preference without any consideration of charge.
(a) Write the IUPAC name of the complex $[Pt(NH_3)_3Br(NO_2)Cl]Cl$.
(b) What is the IUPAC name of $[Ni(CO)_4]$?
(c) Write the name and draw the structures of each of the following complex compounds :
(i) $[Co(NH_3)_4(H_2O)_2]Cl_3$
(ii) $[Pt(NH_3)_4][NiCl_4]$

OR

Using the IUPAC norms, write the systematic name of following :
(i) $[CoCl(NO_2)(NH_3)_4]Cl$
(ii) $[Co(NH_3)_6][Cr(CN)_6]$

LA Type Questions (5 marks)

22. $CoSO_4Cl{\cdot}5NH_3$ exists in two isomeric forms '*A*' and '*B*'. Isomer '*A*' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer '*B*' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$.
Answer the following questions.
(a) Identify '*A*' and '*B*' and write their structural formulae.
(b) Name the type of isomerism involved.
(c) Give the IUPAC names of '*A*' and '*B*'.
23. (a) What are bidentate ligands? Explain with examples.
(b) Explain the coordination sites of polydentate ligands taking an example of EDTA.
(c) Calculate charge on the central metal in the following complexes:
(i) $[Cu(NH_3)_6]^{2+}$ (ii) $[Ag(CN)_2]^-$
24. (a) Explain *cis* and *trans* isomerism in Ma_4b_2 type complexes.
(b) Give example of Ma_3b_3 type complex and draw the structure of its *cis* and *trans* isomers.
25. (a) Explain hybridisation in the complex which contains hexacyanidoferrate(III) ion.
(b) Based on the valence bond theory describe the formation and nature of hexaamminecobalt(III) chloride.
(c) How will you show that hexafluoridocobaltate(III) ion is paramagnetic in nature?

OR

(a) Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following :
(i) $[CoF_6]^{3-}$, (ii) $[FeF_6]^{3-}$, (iii) $[Fe(CN)_6]^{4-}$
(b) $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

Detailed SOLUTIONS

1. **(i) (b) :** $NiCl_2 + 2NH_3 + 2$ dimethylglyoxime $\longrightarrow$ $\left[\begin{matrix}CH_3-C=NOH\\ |\\ CH_3-C=NO^-\end{matrix}\right]_2 Ni$

Rosy red ppt.

(ii) (c) **(iii) (b)**

(iv) (d): It has no unpaired electrons hence, it is diamagnetic.

(v) (d): (a) and (b) are coordination compounds hence cannot give free Fe^{2+} or Fe^{3+} ions in solution.

(c) and (d) represent simple compounds hence are free to give ions in solution, but only $Fe_2(SO_4)_3$ contains Fe^{3+} ions. $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ contains Fe^{2+} ions and not Fe^{3+} ions.

2. **(d):** $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.

3. **(a) :** When a solution of chelating ligand is added to solution containing toxic metals, the ligands chelate the metal ions by formation of stable complex.

4. **(b):** NH_4^+ does not have electron pair to donate to metal ion so, it cannot form coordinate bonds with metal ions.

5. **(c) :** CFSE for tetrahedral complex is

$\Delta_t = (4/9)\Delta_o$

$\Delta_t = \frac{4}{9} \times 18000 = 8000\ cm^{-1}$

6. **(d):** 3 mol of AgCl means $3Cl^-$ ions are given in the solution, hence the formula of the complex will be $[Cr(H_2O)_6]Cl_3$.

7. **(a):** $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are linkage isomers since, SCN^- is an ambidentate ligand and can be linked through S or N.

8. Primary and secondary valencies in (a) are 3 and 6 respectively and in (b) are 2 and 6 respectively.

9. Ionisation isomerism

10. Ligands for which $\Delta_o > P$ are called strong field ligands. *e.g.*, CN^-, CO.

OR

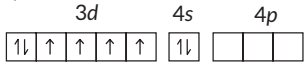
The homoleptic complexes of carbon monoxide (CO) with metals are called metal carbonyls, *e.g.*, $[Ni(CO)_4]$.

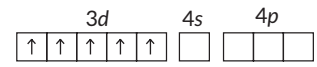
11. Complexes in which metal is bound to only one kind of donor groups are known as homoleptic complexes. *e.g.* $[Co(NH_3)_6]^{3+}$.

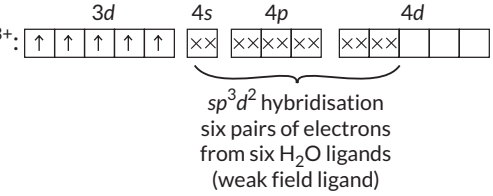
Complexes in which metal is bound to more than one kind of donor groups are called heteroleptic complexes. *e.g.*, $[Co(NH_3)_4Cl_2]^+$.

12. $[Fe(H_2O)_6]^{3+}$:

Fe atom ($Z = 26$)

Ground state : 

Fe^{3+} ion : 

$[Fe(H_2O)_6]^{3+}$: 

The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of five unpaired electrons.

13. (a) $[Co(NH_3)_5Br]SO_4$ will give SO_4^{2-} ion, its name is Pentaamminebromidocobalt(III) sulphate.

Its isomers will be :

$[Co(NH_3)_5SO_4]Br$, Br^- is ionisable, its name is: Pentaamminesulphatocobalt(III) bromide.

(b) $[Pt(NO_2)(H_2O)(NH_3)_2]Br$ will give Br^- ions in solution, its name is diammineaquanitroplatinum(II) bromide. Its isomer will be

$[Pt(H_2O)(NH_3)_2Br]NO_2$, it will give NO_2^- ions in solution, its name is diammineaquabromidoplatinum(II) nitrite.

14. In tetrahedral complexes, all the ligands are arranged in *cis* position with respect to each other, because each ligand is at an equal distance from the other three ligands and therefore, *trans*-isomer does not exist.

15. (i) $[CoCl(NH_3)_5]^{2+}$ (ii) $LiAlH_4$

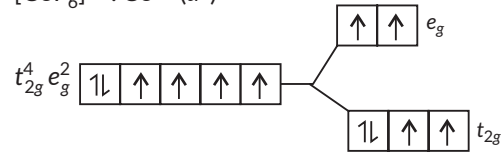
16. In $[Ni(CN)_4]^{2-}$, the oxidation state of Ni is +2, therefore, 8 electrons are present in *d*-orbitals out of which 2 are unpaired. Under the influence of ligand molecules (CN^-) these unpaired electrons are forced to paired and one *d*-orbital becomes vacant before undergoing dsp^2 hybridisation. Four electron pairs from ligand molecules are donated to four dsp^2 hybridised orbitals. As there is no unpaired electron in $[Ni(CN)_4]^{2-}$, therefore, it is diamagnetic in nature having square planar geometry.

OR

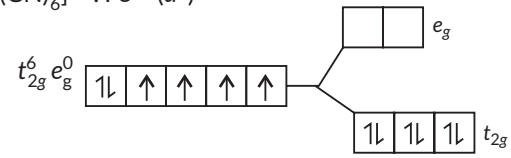
Coordination complexes with a square planar geometry do not show optical isomerism because they contain a plane of symmetry. All the ligands and the metal atom lie in the same plane.

17. Low spin tetrahedral complexes are not formed because for tetrahedral complexes the CFSE is lower than pairing energy hence, pairing of electrons does not take place.

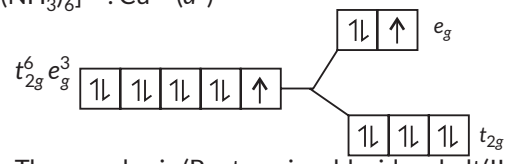
18. $[CoF_6]^{3-}$: Co^{3+} (d^6)



$[Fe(CN)_6]^{4-}$: Fe^{2+} (d^6)



$[Cu(NH_3)_6]^{2+}$: Cu^{2+} (d^9)



19. The complex is (Pentaaminechloridocobalt(III) chloride) *i.e.*, $[Co(NH_3)_5Cl]Cl_2$

Only primary valencies are ionised.

$$[Co(NH_3)_5\,Cl]Cl_2 \rightleftharpoons \underbrace{[Co(NH_3)_5\,Cl]^{2+} + 2Cl^-}_{\text{3 ions}}$$

$$2AgCl + [Co(NH_3)_5\,Cl](NO_3)_2 \xleftarrow{(2AgNO_3)}$$

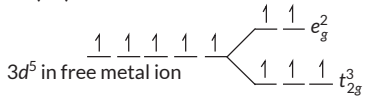
20. (i) Anhydrous $CuSO_4$ has no ligand or H_2O molecules. So, crystal, field splitting does not occur so, it does not show any colour but in hydrated form it is linked with H_2O ligand so, it shows colour due to *d-d* transition.

(ii) $[Ti(H_2O)_6]Cl_3$ is a complex compound. In presence of $6H_2O$ molecules the *d*-orbitals of Ti^{3+} undergo splitting. The compound is coloured (violet) due to *d-d* transition. On heating, water molecules escape, *d*-orbitals become degenerate. There is no *d-d* transition. Hence, compound becomes colourless.

OR

$[FeF_6]^{3-}$,

Fe(III) – $3d^5$ and F^- is a weak field ligand

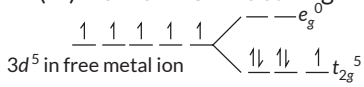


In weak octahedral crystal field

So, it has 5 unpaired electrons.

In $[Fe(CN)_6]^{3-}$,

Fe (III) – $3d^5$ and CN^- is strong field ligand.



In strong octahedral field

It has one unpaired electron.

21. (a) Ligands are named in an alphabetical order irrespective of their charge,

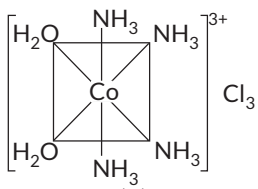
triamminebromidochloridonitroplatinum(IV) chloride.

(b) tetracarbonylnickel(0)

(c) (i) Tetraamminediaquacobalt (III) chloride

$[Co(NH_3)_4(H_2O)_2]Cl_3$

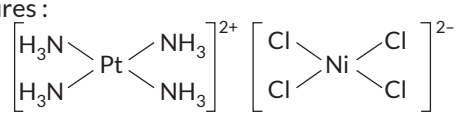
Structure :



(ii) Tetraammineplatinum (II) tetrachloridonickelate(II)

$[Pt(NH_3)_4]^{2+}\,[NiCl_4]^{2-}$

Structures :



OR

(i) Tetramminechloridonitrito-N-cobalt(III) chloride

(ii) Hexamminecobalt(III)hexacyanidochromate(III)

22. $CoSO_4Cl{\cdot}5NH_3$:

(a) Isomer *A* reacts with $AgNO_3$ but not with $BaCl_2$, it shows it has Cl^- ion outside the coordination sphere.

Hence, *A* = $[Co(NH_3)_5SO_4]Cl$

Isomer *B* reacts with $BaCl_2$ but not with $AgNO_3$, it shows it has SO_4^{2-} outside the coordination sphere.

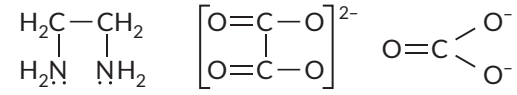
Hence, *B* = $[Co(NH_3)_5Cl]SO_4$

(b) Ionisation isomerism

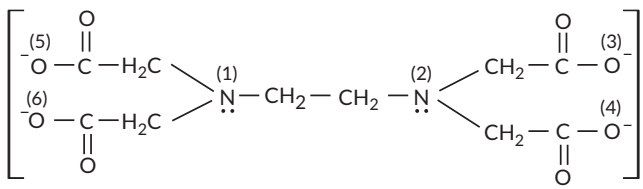
(c) *A* = Pentaamminesulphatocobalt (III) chloride and

B = Pentamminechloridocobalt (III) sulphate

23. (a) Ligands which can coordinate with the central metal atom or ion through two donor atoms are known as bidentate ligands. Examples of bidentate ligands are:



(b) Ligands which coordinate with the central ion through more than two donor atoms present in the molecule are called polydentate ligands. These are tridentate(three), tetradentate(four), pentadentate(five) and hexadentate (six) ligands depending upon the number of coordinating donor atoms present in their molecules. A common example of hexadentate ligand is ethylenediamminetetraacetate ion as shown below:

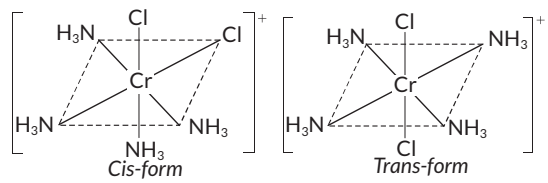


(c) The charge carried by a complex ion is the algebraic sum of charges carried by the central metal ion and the ligands coordinated to it.

(i) $[Cu(NH_3)_6]^{2+}$ carries a charge of +2 because Cu^{2+} carries a charge of +2 and ammonia molecule is neutral.

(ii) $[Ag(CN)_2]^-$ ion carries a charge of −1 because Ag carries a charge of +1 and two cyanide ions coordinated to it carry a charge of −1 each.

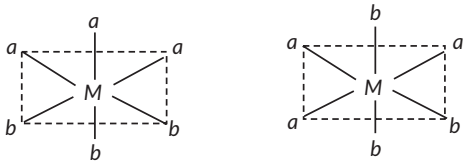
24. (a) Complex of the type Ma_4b_2 shows *cis* and *trans* geometrical isomerism. For example, the structures of *cis* (violet) and *trans* (green) forms of tetraamminedichloridochromium (III) ion are shown as-



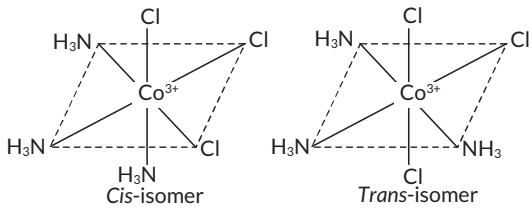
cis and *trans* forms of $[CrCl_2(NH_3)_4]^+$ complex

(b) For a compound of the type Ma_3b_3, the three groups may all be adjacent *i.e.* at the corners of one face of the

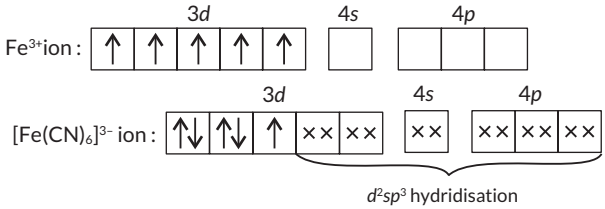
octahedron or they may occupy three positions such that two are *trans* to each other: (a) and (b) are shown respectively.



Examples of this type are $[Co(NH_3)_3Cl_3]$.

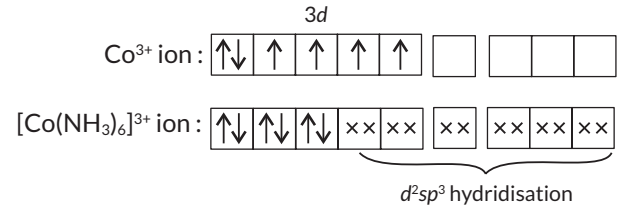


25. (a) Formation of hexacyanidoferrate(III) ion; $[Fe(CN)_6]^{3-}$: Electronic configuration of iron in the ground state is $3d^6 4s^2$. The oxidation state of iron is +3 in this complex. Iron (III) has outer electronic configuration $3d^5 4s^0$. It has been experimentally observed that this complex has one unpaired electron. To account for this, two unpaired electrons in 3*d* subshell pair up, thus leaving two 3*d*-orbitals empty. These two vacant 3*d*-orbitals, along with one 4*s*-orbital and three 4*p*-orbitals hybridise to give six equivalent d^2sp^3 hybridised orbitals. Six pairs of electrons, one from each cyanide ion, occupy the six vacant hybrid orbitals so produced. The complex has octahedral geometry and is paramagnetic due to the presence of one unpaired electron.

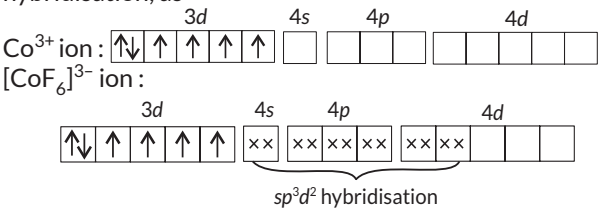


The complex evidently involves $(n-1)d^2\, ns\, np^3$ hybridisation and is, therefore, called inner orbital or low spin complex.

(b) The outer electronic configuration of cobalt (III) ion is $3d^6$. According to Hund's rule, four of the 3*d*-orbitals are singly filled and one 3*d*-orbital has a pair of electrons. Octahedral complexes are formed through d^2sp^3 hybridisation for which the metal atom must have two of its 3*d*-orbitals empty. This is achieved by the pairing of the two 3*d*-electrons as a result of the energy released due to the approach of the ligands. This results in the formation of an octahedral complex. As it is evident from the figure given below, the complex does not contain any unpaired electron and is, therefore, diamagnetic.



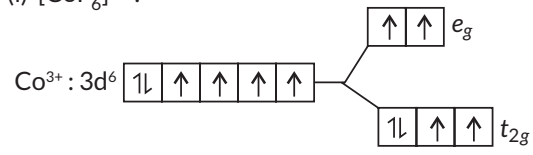
(c) In $[CoF_6]^{3-}$ complex, the 3*d*-orbitals remain undisturbed while the outer 4*d*-orbitals are used for hybridisation, as



The complex is paramagnetic since it contains four unpaired electrons.

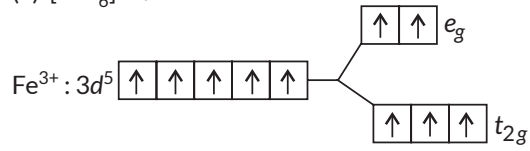
OR

(a) (i) $[CoF_6]^{3-}$:



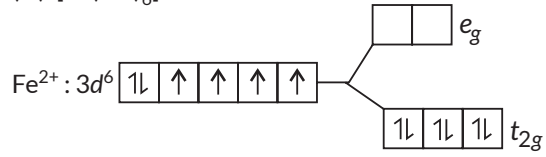
No. of unpaired electrons = 4, $\mu = \sqrt{4(4+2)} = 4.9$ B.M.

(ii) $[FeF_6]^{3-}$:



No. of unpaired electrons = 5, $\mu = \sqrt{5(5+2)} = 5.92$ B.M.

(iii) $[Fe(CN)_6]^{4-}$:



No. of unpaired electrons = 0, $\mu = 0$

(b) When $FeSO_4$ and $(NH_4)_2SO_4$ solutions are mixed in 1 : 1 molar ratio, Mohr's salt (a double salt) is formed.

$FeSO_{4(aq)} + (NH_4)_2SO_{4(aq)} \rightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \rightleftharpoons Fe^{2+}_{(aq)} + 2NH^{+}_{4(aq)} + 2SO^{2-}_{4(aq)} + 6H_2O$

Because Fe^{2+} ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of Fe^{2+} ions.

When $CuSO_4$ is mixed with ammonia, following reaction occurs :

$CuSO_{4(aq)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]SO_4$

This complex does not produce Cu^{2+} ion, so the solution of $CuSO_4$ and NH_3 does not give the test of Cu^{2+} ion.

CHAPTER

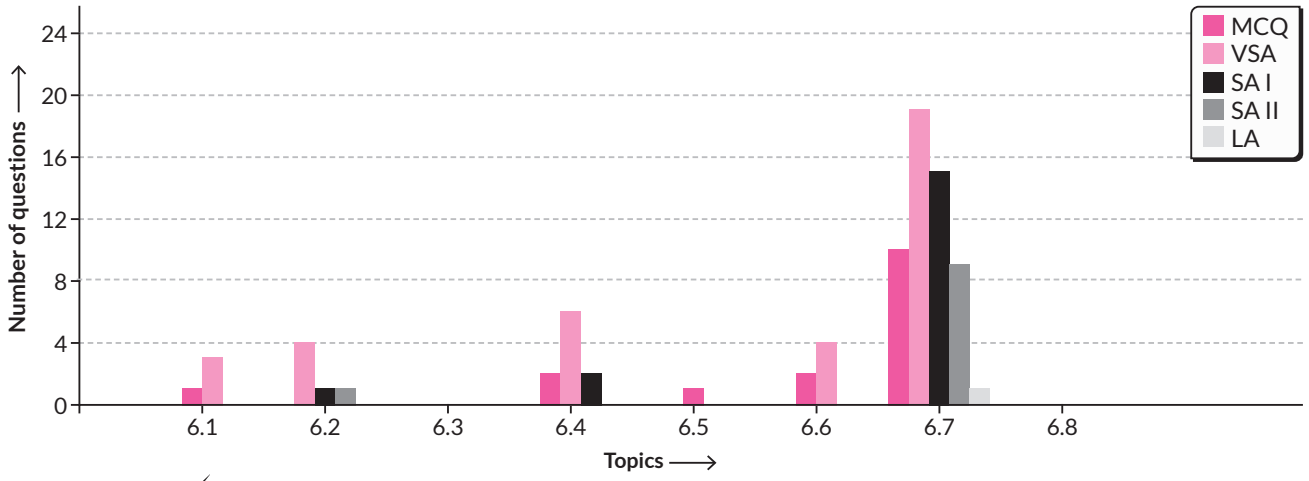
6

Haloalkanes and Haloarenes

TOPICS

6.1 Classification
6.2 Nomenclature
6.3 Nature of C—*X* Bond
6.4 Methods of Preparation of Haloalkanes
6.5 Preparation of Haloarenes
6.6 Physical Properties
6.7 Chemical Reactions
6.8 Polyhalogen Compounds

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topic 6.7 is highly scoring topic.
- Maximum total weightage is of Topic 6.7 *Chemical Reactions*.
- Maximum MCQ, VSA, SA I, SA II type questions were asked from Topic 6.7 *Chemical Reactions*.

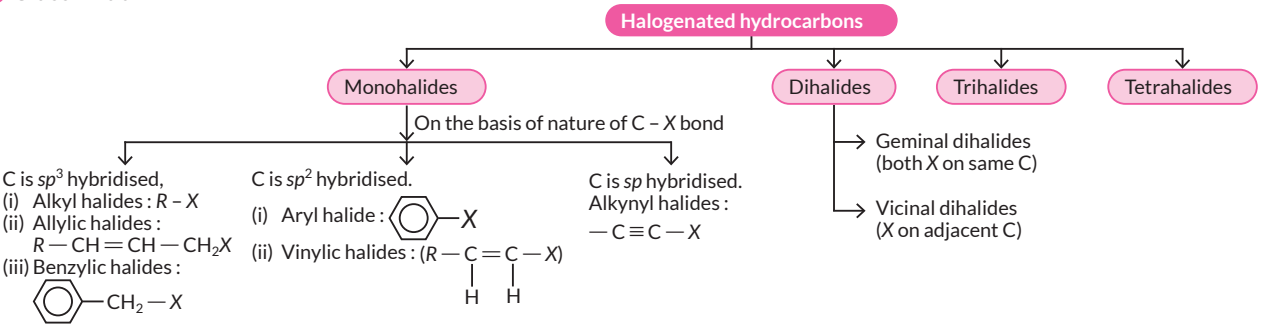
QUICK RECAP

Haloalkanes and haloarenes : The replacement at hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene) respectively.

Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group. Many halogen containing organic compounds occur in nature and some of these are clinically useful.

These classes of compounds find wide applications in industry as well as in day-to-day life.

Classification :


Halogenated hydrocarbons
Monohalides
Dihalides
Trihalides
Tetrahalides
On the basis of nature of C – X bond
C is sp3 hybridised,
(i) Alkyl halides : R – X
(ii) Allylic halides :
R — CH = CH — CH2X
(iii) Benzylic halides :
CH2 — X
C is sp2 hybridised.
(i) Aryl halide : X
(ii) Vinylic halides : (R — C = C — X)
H H
C is sp hybridised.
Alkynyl halides :
— C ≡ C — X
Geminal dihalides
(both X on same C)
Vicinal dihalides
(X on adjacent C)

HALOALKANES

Alkyl halides : General formula is *RX*, where *R* = alkyl group.

General methods of preparation :

- **From alcohols :** Alkyl halides can be prepared from alcohols in a number of ways :
  - **Action of hydrogen halides :**

$$R-OH \xrightarrow{HCl/\text{anhyd. } ZnCl_2} R-Cl + H_2O$$
$$R-OH \xrightarrow[\text{or KBr + conc. } H_2SO_4, \text{ reflux}]{HBr/H_2SO_4, \text{ reflux}} R-Br + H_2O$$
$$R-OH \xrightarrow[\text{or KI + } H_3PO_4, \text{ reflux}]{HI \text{ reflux}} R-I + H_2O$$

  - Order of reactivity of halogen acids towards the above reaction is : HI > HBr > HCl
  - Order of reactivity of different alcohols towards the above reaction is : tertiary > secondary > primary
  - **Action of phosphorus halides :**

$$R-OH \xrightarrow{PCl_5} R-Cl + POCl_3 + HCl$$
$$R-OH \xrightarrow{PCl_3} R-Cl + H_3PO_3$$
$$R-OH \xrightarrow[(P + Br_2)]{PBr_3} R-Br + H_3PO_3$$
$$R-OH \xrightarrow[(P + I_2)]{PI_3} R-I + H_3PO_3$$

  - **Action of thionyl chloride (Darzen's process) :**

$$R-OH + SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl + SO_2\uparrow + HCl\uparrow$$

- **Halogenation of alkanes :**

$$R-H + X_2 \xrightarrow[\text{or } 250\text{-}400^\circ C]{h\nu} RX + HX$$

  - Abstraction of hydrogen for a particular halogen follows the order :
    allylic > 3° > 2° > 1° > CH_4
  - Reactivity of halogens for the above reaction follows the order : $F_2 > Cl_2 > Br_2 > I_2$

- **Halide exchange method :**

$$R-Cl + NaI \xrightarrow{\text{dry acetone}} R-I + NaCl$$

  This is known as *Finkelstein reaction*.
  - Fluoroalkanes can also be prepared by halide exchange method by reacting alkyl chloride with inorganic fluorides. This is known as *Swarts reaction*.

$$2CH_3CH_2Cl + Hg_2F_2 \rightarrow 2CH_3CH_2F + Hg_2Cl_2$$
(Mercurous fluoride; Mercurous chloride)

- **Action of hydrogen halides on ethers :**

$$R-O-R + 2HX \longrightarrow 2R-X + H_2O$$

- **Addition of hydrogen halides to alkene :**
  Alkenes add a molecule of hydrogen halide to form alkyl halide.

$$>C=C< + HX \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-$$
$$CH_3-CH=CH_2 + HCl \longrightarrow CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$$

  - Reaction follows electrophilic addition mechanism and takes place as per Markownikoff's rule. However, in presence of peroxide, addition of HBr takes place as per anti-Markownikoff's rule.

$$CH_3-CH=CH_2 + HBr$$
Absence of peroxide: $CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$ (Markownikoff's addition)
Presence of peroxide: $CH_3-CH_2-CH_2Br$ (Anti-Markownikoff's addition)

Anti-Markownikoff's rule is also known as *Peroxide effect* or *Kharasch effect*. HCl and HI do not show peroxide effect.

Physical properties :

- Alkyl halides being polar in nature are insoluble in water as they cannot break H-bonding already existing in water.
- They have higher melting and boiling points, than those of the hydrocarbons of comparable molecular mass. For the same alkyl group boiling point follows the order as :
  R—I > *R*—Br > *R*—Cl > *R*—F
- Decreasing order of boiling points among the isomeric alkyl halides follows the order:
  1° > 2° > 3° alkyl halides
- Decreasing order of density among the alkyl halides is *R*I > *R*Br > *R*Cl > *R*F.
  Density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.
- Bond strength of C—*X* bond follows the order :
  CH_3—F > CH_3—Cl > CH_3—Br > CH_3—I
  i.e., bond strength of C—*X* bond decreases as the size of halogen atoms increases.
- Correct stability order of *RX* is as follows :
  R—F > *R*—Cl > *R*—Br > *R*—I

Chemical properties :

- **Nucleophilic substitution reactions :** The reactions in which a stronger nucleophile displaces a weaker nucleophile are called nucleophilic substitution reactions. Better the leaving group, more facile is the nucleophilic substitution reaction.
- **S_N1 and S_N2 mechanisms :** The nucleophilic substitution can proceed via S_N1 mechanism or S_N2 mechanism.

Unimolecular (S_N1)	Bimolecular (S_N2)
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile or DMF.
Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : 3° > 2° > 1° > CH_3 halides (fastest) (slowest) Greater the stability of carbocation, faster will be the reaction.	Rate of reaction : CH_3 > 1° > 2° > 3° halides (fastest) (slowest) Less the steric hindrance in transition state, faster will be the reaction.

Tends to proceed with weak nucleophiles, *e.g.*, CH_3OH, H_2O, CH_3CH_2OH, etc.	Tends to proceed with strong nucleophiles, *e.g.*, CH_3O^-, CN^-, OH^-, etc.
Both retention and inversion of configuration takes place.	Inversion of configuration takes place (Walden inversion).

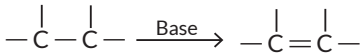
- Primary allylic and primary benzylic halides show higher reactivity in S_N1 reactions than other primary alkyl halides due to the greater stabilisation of allylic and benzylic carbocation intermediates by resonance.
- Vinylic and aryl halides are unreactive in nucleophilic substitution reactions. This is because of double bond character of C — *X* bond due to resonance.

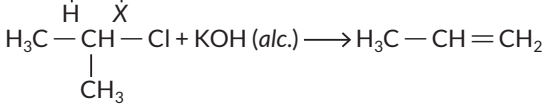
Optical isomerism/Enantiomerism :

- Optical isomer is known as *dextrorotatory isomer* (latin : *dexter* means right) (*d*-form or +ve), it rotates the plane polarised light to the right (clockwise) and *laevorotatory isomer* (latin : *laevo* means left) (*l*-form or –ve), it rotates the plane polarised light to the left (anticlockwise).
- An equimolar mixture of the *d*-form and *l*-form will be optically inactive and is called *racemic mixture* (or *dl- form or* (±)-*mixture*).
- The process of conversion of an enantiomer into racemic mixture is known as *racemisation*.
- **Chirality :** The compound is said to have chirality if the central carbon atom is attached to four different groups and this centre is called *chiral* (*asymmetric*) *centre* or *stereogenic centre* or *stereocentre*.
- **Achirality :** The compound is said to have achirality if the central carbon atom have atleast two identical groups and this centre is called *achiral* (*symmetric*).
- If molecule has a plane of symmetry it is *achiral* (*not chiral*) and if molecule has no plane of symmetry it is *chiral*.
- **Enantiomers/*d*- and *l*-isomers :** They are the optical isomers which are non-superimposable mirror images (or assymmetric).
- **Diastereomers :** They are the optical isomers which are non mirror images of each other. They have different physical properties and magnitude of specific rotation.
- **Meso compounds :** These compounds have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal compensation.

Elimination reactions:

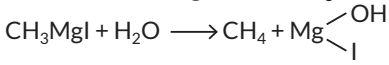
- **Dehydrohalogenation :**



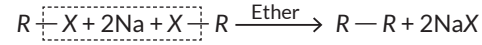


Reaction with metals:

- **Reaction with Mg metal :** $CH_3I + Mg \xrightarrow{Ether} CH_3MgI$



- **Wurtz reaction :**



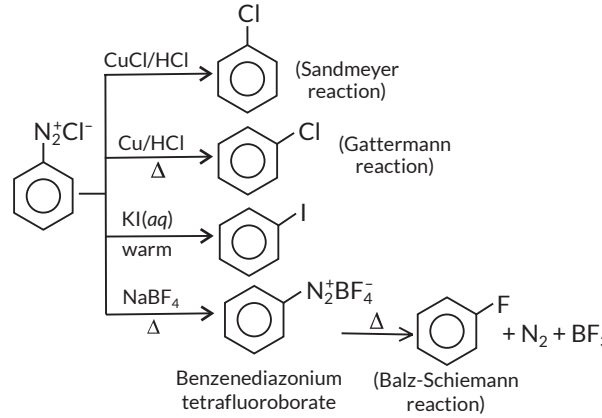
Reduction of alkyl halides :

HALOARENES

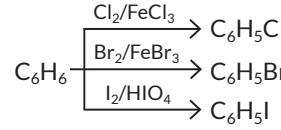
Aryl halides : General formula is Ar*X*, where Ar = aryl group.

General methods of preparation :

- **From benzenediazonium salt :**



- **By direct halogenation of benzene :**

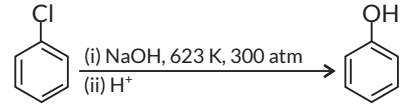


Physical properties :

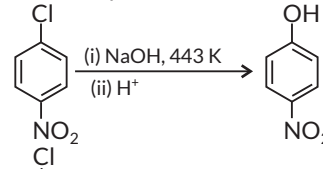
- Aryl halides are colourless stable liquids with pleasant odour.
- These are insoluble in water but readily miscible with organic solvents.
- Most of them are steam volatile, heavier than water.
- Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from fluoro to iodo compounds.

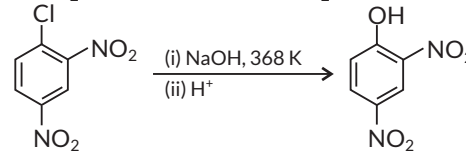
Chemical properties :

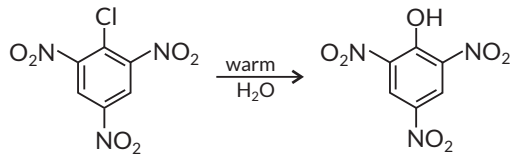
- **Nucleophilic substitution reactions :**



The presence of an electron withdrawing group (—NO_2) at *ortho*- and *para*-positions increases the reactivity of haloarenes.

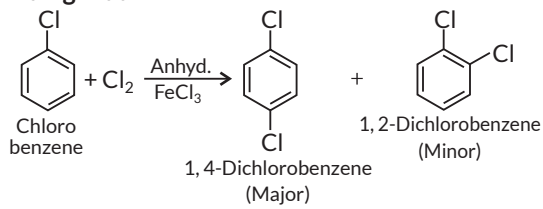




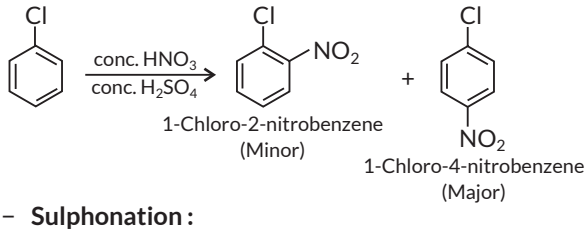


▶ **Electrophilic substitution reactions :**

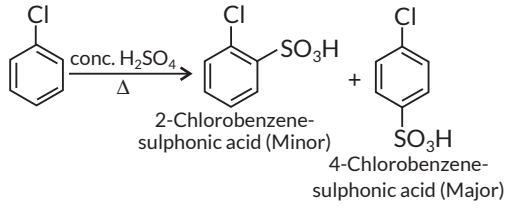
– **Halogenation :**



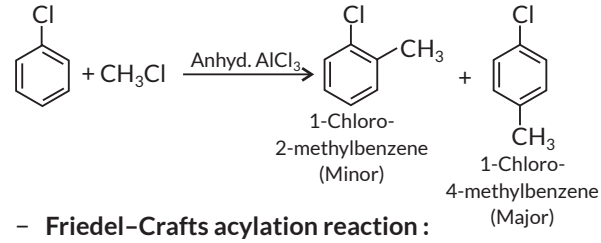
– **Nitration :**



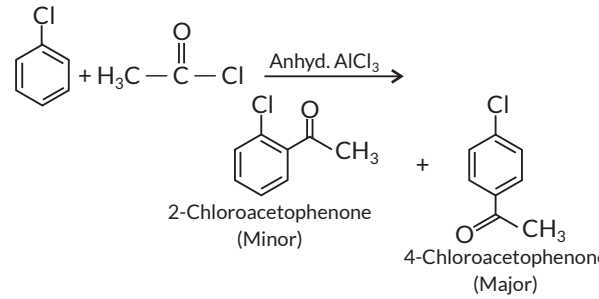
– **Sulphonation :**



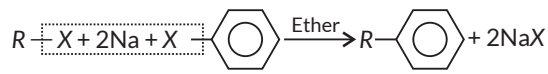
– **Friedel–Crafts alkylation reaction :**



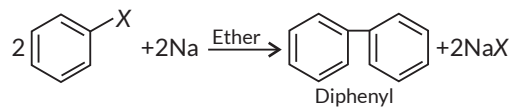
– **Friedel–Crafts acylation reaction :**



▶ **Wurtz-Fittig reaction :**



▶ **Fittig reaction :**



Uses and environmental effects of some important compounds :

Compounds	Uses	Effects
Chloroform ($CHCl_3$)	– It is used in the production of freon refrigerant, R-22. – It is used as a solvent for resins, rubbers, oils and fats, alkaloids, iodine and many other substances. – Earlier, it was extensively used as anaesthetic for surgery but is no more used as it causes liver damage. – It is used in preparation of chloretone (drug) and chloropicrin (insecticide). – It is used to preserve anatomical species.	– It is oxidised to poisonous gas, carbonyl chloride, known as *phosgene* which causes liver and kidney damage. $2CHCl_3 + O_2 \xrightarrow{Light} 2COCl_2 + 2HCl$ – Inhaling vapours of $CHCl_3$ depresses the central nervous system, causes dizziness, fatigue and headache.
Iodoform (CHI_3)	– It was earlier used as an antiseptic in dressing of wounds due to liberation of iodine. Due to its objectionable smell, it has been replaced by other formulations containing iodine. – It is used as methylating agent in organic synthesis.	– It has strong smell.
Carbon tetrachloride (CCl_4)	– It is used in the manufacture of refrigerants and propellants for aerosol cans. – It is used as feed stock in the synthesis of CFC's and other chemicals.	– Exposure to CCl_4 causes liver cancer. – It causes dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. – It deplets the ozone layer.
Freons	– They are used as refrigerants, blowing agents, propellants in medical applications and degreasing solvent.	– Freons cause disruption of ozone layer by initiating radical chain reactions in stratosphere. – This anthropogenic compound is a greenhouse gas and its effect is more than CO_2.
DDT	– In 1940, it was used as a pesticide.	– It is a persistent organic pollutant, strongly absorbed by soil. – It is lipophilic so has a high potential to bioaccumulate.

HALOALKANES AND HALOARENES

Halogen Derivatives
Obtained by replacing one or more H-atoms of hydrocarbons.

Haloalkanes

Properties

Physical

- Water insoluble
- **M.Pt. and B.Pt. :** R–I > R–Br > R–Cl > R–F
- B.Pt. ∝ alkyl part size
- B.Pt. ∝ 1/branching
- **Bond strength :** CH_3–F > CH_3–Cl > CH_3–Br > CH_3–I
- **Stability of C–X bond :** R—F > R–Cl > R–Br > R–I

Chemical

- Highly reactive

Nucleophilic Substitution Reaction

S_N1 : I order reaction :

- Rate ∝ [substrate]
- Proceeds *via* carbonium ion formation.
- In 2 steps, I → formation of carbonium ion (slow → rate determining), II → Attack of nucleophile.
- Racemic mixture obtained.
- Most favourable substrate → 3° alkyl halide.

S_N2 : II order reaction :

- Rate ∝ [alkyl halide] [nucleophile]
- Concerted reaction (in 1 step).
- Inversion of configuration occurs (Walden inversion).
- Most favourable substrate → 1° alkyl halide.
- Favoured in non-polar solvent.

Optical Isomerism

Substances which can rotate the plane of polarized light → optically active.
Dextrorotatory (+) → rotates towards right.
Laevorotatory (–) → rotates towards left.

- Stereoisomers having non super-imposable mirror images are optically active and these are called *enantiomers.*
- Stereoisomers that are not mirror images of each other are called *diastereomers.*
- If both *d* and *l* enantiomers present in equal amount (50-50%) then the mixture is optically inactive due to external compensation, the mixture is known as *racemic mixture.*
- If plane of symmetry is present in the molecule then, one of the isomer will be optically inactive due to internal compensation because half of the molecule will rotate the plane polarised light towards right and another half towards left. So, total rotation of plane polarised light will be zero, these are called meso compounds.

Haloarenes

Properties

Physical

- B.Pt. iodoarenes > bromoarenes > chloroarenes > fluoroarenes.
  B.Pt. isomeric dihalobenzenes → nearly same.
- M.Pt. of isomeric dihalobenzenes → $p > o > m$

Chemical

- Low reactivity due to lesser polar character.
- C–X bond acquires some double bond character and hence stronger.
- Presence of e^- withdrawing groups such as –NO_2, –CN etc. at o– and p– positions w.r.t. halogen → activates the halogen towards nucleophilic displacement.
- Halogen atom is slightly deactivating and o, p–directing (p-product usually predominates).

Elimination Reaction

E1 : In 2 steps.
- Reactivity of alkyl halides : 3° > 2° > 1°

E2 : In 1 step
- *via* transition state.
- Favourable → 1° alkyl halide.

R–X + Mg $\xrightarrow{\text{dry ether}}$ R–Mg–X (Grignard's reagent)

R–X + NaCN $\xrightarrow[\Delta]{C_2H_5OH-H_2O}$ R–C≡N

R–X + AgCN ⟶ R–N≡C

R–I + $AgNO_2$ $\xrightarrow[-AgI]{\text{Alcohol, }\Delta}$ RNO_2 (Nitro alkane)

R–X + $R'ONa$ ⟶ ROR' + NaX

Polyhalogen Compounds

Dihalogens

Compounds with two halogen atoms

Vicinal dihalides

Both halogen atoms on different atoms

Geminal dihalides

Both halogen atoms on same carbon atom

Trihalogens

Compounds with three halogen atoms *e.g.* $CHCl_3$, CHI_3

Chlorofluorocarbons

Freons

Polychlorofluoro alkanes - CCl_2F_2, $C_2Cl_2F_4$

Perfluorocarbons (PFC)

C_nF_{2n+2}, CF_4, C_2F_6

BHC

Gammexane C_6H_6Cl

BRAIN MAP

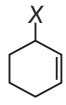
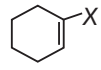
Previous Years' CBSE Board Questions

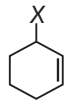
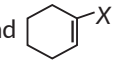
6.1 Classification

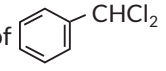
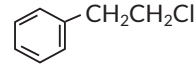
MCQ

1. Which one of the following halides contains $C_{sp^2}-X$ bond?
   (a) Allyl halide (b) Alkyl halide
   (c) Benzyl halide (d) Vinyl halide
   (Term I, 2021-22) Ap

VSA (1 mark)

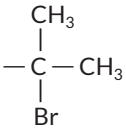
2. Out of  and  , which is an example of allylic halide? *(AI 2017)*

3. Out of  and  , which is an example of vinylic halide? *(AI 2017)*

4. Out of  and  , which is an example of a benzylic halide? *(AI 2017)* U

6.2 Nomenclature

VSA (1 mark)

5. Write the IUPAC name of 
   (AI 2019, Delhi 2013)

6. Write the structure of 1-bromo-4-chlorobut-2-ene. *(Delhi 2017)*

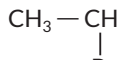
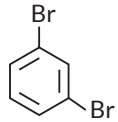
7. Write the structure of 3-bromo-2-methylprop- 1-ene. *(Delhi 2017)* U

8. Draw the structure of 2-bromopentane. *(Delhi 2014C)*

SA I (2 marks)

9. Write the IUPAC names of the following compounds :
   (i) $CH_2=CHCH_2Br$
   (ii) $(CCl_3)_3CCl$ *(AI 2014C)*

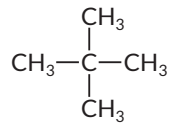
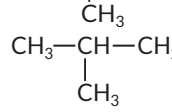
SA II (3 marks)

10. Give the IUPAC names of the following compounds :
    (i) 
    (ii) 
    (iii) $CH_2=CH-CH_2-Cl$ *(AI 2015C)* Ap

6.4 Methods of Preparation of Haloalkanes

MCQ

11. The synthesis of alkyl flouride is best obtained from
    (a) Free radicals (b) Swarts reaction
    (c) Sandmeyer reaction (d) Finkelstein reaction.
    (2023)

12. Which of the following isomer of pentane (C_5H_{12}) will give three isomeric monochlorides on photochemical chlorination?
    (a)  (b) $CH_3CH_2CH_2CH_2CH_3$
    (c)  (d) All of the above.
    (Term I, 2021-22) An

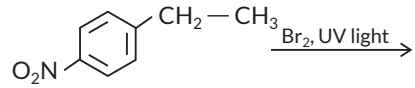
VSA (1 mark)

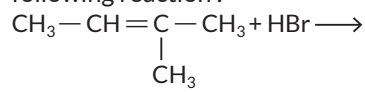
13. How can you convert the following?
    But-1-ene to 1-iodobutane *(NCERT, 1/3, 2020)* An

14. Give reason for the following :
    Thionyl chloride method is preferred for preparing alkyl chloride from alcohols. *(1/3, AI 2019)* U

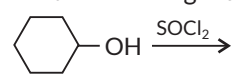
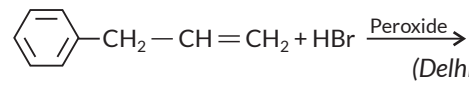
15. Write equation for preparation of 1-iodobutane from 1-chlorobutane. *(1/3, AI 2019)*

16. How do you convert :
    Propene to 1-iodopropane? *(1/3, AI 2016)*

17. Write the major product in the following :
    
    (1/3, AI 2016)

18. Write the structure of the major product in the following reaction :
    
    (1/3, AI 2015)

SA I (2 marks)

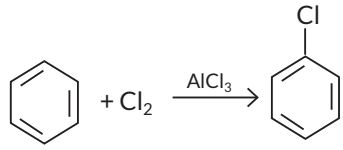
19. Draw the structure of major monohalo product in each of the following reactions :
    (i) 
    (NCERT)
    (ii) 
    (Delhi 2014)

20. Write the mechanism of the following reaction :
    $CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$ *(AI 2014)*

6.5 Preparation of Haloarenes

MCQ

21. The species that attacks benzene in following is



(a) Cl^- (b) $AlCl_4^-$ (c) $AlCl_3$ (d) Cl^+ *(2023)*

6.6 Physical Properties

MCQ

22. Which of the following has highest boiling point?
(a) $C_2H_5—F$ (b) $C_2H_5—Cl$
(c) $C_2H_5—Br$ (d) $C_2H_5—I$ *(Term I, 2021-22)*

23. **Assertion (A) :** Boiling points of alkyl halides decrease in the order *R*-*I* > *R*-Br > *R*-Cl > *R*-F.
Reason (R) : van der Waals' forces decrease with increase in the size of halogen atom.
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(2020)*

VSA (1 mark)

24. Give reason for the following :
p-dichlorobenzene has higher melting point than that of *ortho* or *meta* isomer. *(1/3, AI 2019)*

25. Explain the following :
Alkyl halides, though polar, are immiscible with water. *(NCERT, 1/2, AI 2017C, 1/3, Foreign 2015)*

26. Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. *(NCERT, 1/3, Delhi 2016)*

27. Give reason : *n*-Butyl bromide has higher boiling point than *t*-butyl bromide. *(1/3, Delhi 2015)* U

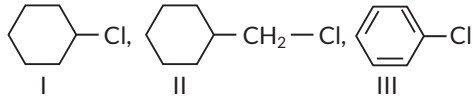
6.7 Chemical Reactions

Nucleophilic Substitution Reactions

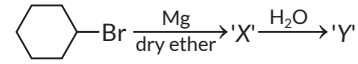
MCQ

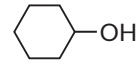
28. Which of the following molecules has a chiral centre correctly labelled with an asterisk(*)?
(a) $CH_3C^*HBrCH_3$
(b) $CH_3C^*HClCH_2Br$
(c) $HOCH_2C^*H(OH)CH_2OH$
(d) $CH_3C^*Br_2CH_3$ *(2023)*

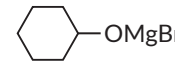
29. Consider the following compounds

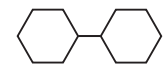


the correct order of reactivity towards S_N2 reaction
(a) I > III > II (b) II > III > I
(c) II > I > III (d) III > I > II *(Term I, 2021-22)*

30. In the reaction, 

compound '*Y*' is
(a) 

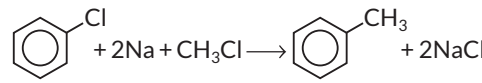
(b) 

(c)
(d) 
(Term I, 2021-22) An

31. Enantiomers differ only in
(a) boiling point
(b) rotation of polarised light
(c) melting point
(d) solubility. *(Term I, 2021-22)* R

32. **Assertion (A) :** Chlorobenzene is less reactive towards nucleophilic substitution reaction.
Reason (R) : Nitro group in chlorobenzene increases its reactivity towards nucleophilic substitution reaction.
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true and R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(Term I, 2021-22)* U

33. The reaction given below:



is called
(a) Wurtz reaction (b) Wurtz-Fitting reaction
(c) Fitting reaction (d) None of the above *(2021 C)*

34. Racemisation occurs in
(a) S_N2 reaction
(b) S_N1 reaction
(c) neither S_N2 nor S_N1 reaction
(d) S_N2 reaction as well as S_N1 reaction. *(2020)* R

35. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as
(a) a dehydrohalogenation reaction
(b) a substitution reaction
(c) an addition reaction
(d) a dehydration reaction *(2020)* U

36. Out of the following, the one which is most reactive towards nucleophilic substitution reaction is
(a) $CH_2=CH—Cl$
(b) $C_6H_5—Cl$
(c) $CH_3CH=CH—Cl$
(d) $CH_3-CH_2-CH_2-Cl$ *(2020 C)*

VSA (1 mark)

Read the passage given below and answer the following questions (Q. No. 37 to 41) :

The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions are governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

37. Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.

38. Name the instrument used for measuring the angle by which the plane polarised light is rotated.

39. Predict the major product formed when 2-bromopentane reacts with alcoholic KOH.

40. Give one use of CHI_3.

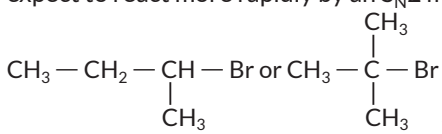
41. Write the structures of the products formed when anisole is treated with HI. *(2020)*

42. Out of and , which will react faster in S_N1 reaction with OH^-? *(One word, 2020)*

43. Why is *t*-butyl bromide more reactive towards S_N1 reaction as compared to *n*-butyl bromide ? *(2019)*

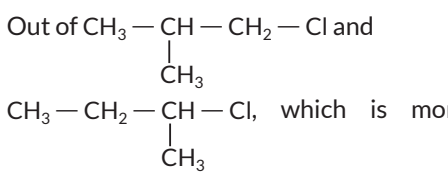
44. Out of chlorobenzene and cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why ? *(2019)*

45. Which alkyl halide from the following pair would you expect to react more rapidly by an S_N2 mechanism?



(AI 2019) An

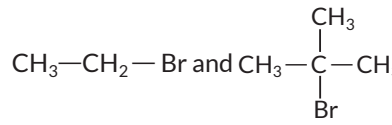
46. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? *(2018)* An

47. Out of 

towards S_N1 reaction and why? *(Delhi 2016)*

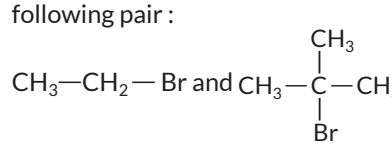
48. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards S_N1 reaction. *(AI 2016)*

49. Which would undergo S_N2 reaction faster in the following pair and why?



(Delhi 2015)

50. Which would undergo S_N1 reaction faster in the following pair :

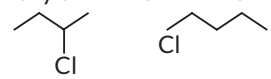


(AI 2015)

51. Which would undergo S_N2 reaction faster in the following pair and why?

$CH_3—CH_2—Br$ and $CH_3—CH_2—I$ *(Foreign 2015)*

52. Identify the chiral molecule in the following pair :



(AI 2014)

53. Which halogen compound in each of the following pairs will react faster in S_N2 reaction :

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

(AI 2014, Delhi 2014C)

SA I (2 marks)

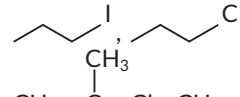
54. (a) $CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3 \xrightarrow{PCl_5} 'A' \xrightarrow{AgCN} 'B'$

(b) $CH_3CH_2CH_2Cl + KOH \xrightarrow{\text{ethanol}} 'A' \xrightarrow{HBr} 'B'$

(2023)

55. Why haloarenes are not reactive towards nucleophilic substitution reaction? Give two reasons. *(2023)*

56. In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?
Given reason in support of your answer.

(i) 

(ii) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}—Cl$, $CH_3—CH_2—Cl$ *(2021 C)*

57. Write the mechanism of the following S_N1 reaction.

$(CH_3)_3C—Br \xrightarrow{aq.\ NaOH} (CH_3)_3C—OH + NaBr$

(2/3, 2020)

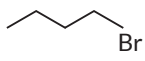
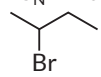
58. Give reasons:
(i) Racemic mixture is optically inactive.
(ii) The presence of nitro group ($—NO_2$) at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.
(AI 2019, 2/3, Delhi 2015)

59. Give reasons :
(i) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in $CH_3—Cl$.
(ii) S_N1 reactions are accompanied by racemization in optically active alkyl halides.
(2/3, Delhi 2016) Ap

60. How do you convert?
(i) Chlorobenzene to Biphenyl
(ii) 2-Bromobutane to but-2-ene *(2/3, AI 2016)*

61. (i) Why is butan-1-ol optically inactive but butan-2-ol is optically active?
(ii) Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Why? *(2/3, Foreign 2015)*

62. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(a)  (b) 

(ii) Out of S_N1 and S_N2, which reaction occurs with
(a) inversion of configuration
(b) racemisation? *(2/3, Delhi 2014)* An

63. (i) Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism and why?

$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$,

$CH_3-CH_2-CH_2-CH_2-Br$

(ii) Racemisation occurs in S_N1 reactions. Why? *(Foreign 2014)* An

64. What are ambident nucleophiles? Explain with an example. *(2/3, AI 2014C)* R

SA II (3 marks)

65. Write main product formed when
(a) Methyl chloride is treated with NaI/Acetone.
(b) 2,4,6-trinitrochlorobenzene is subjected to hydrolysis.
(c) *n*-Butyl chloride is treated with alcoholic KOH. *(2023)*

66. Give reasons :
(a) Grignard reagent should be prepared under anhydrous conditions,
(b) Alkyl halides are immiscible with water although they are polar, and
(c) Chloroform is stored in dark coloured bottles filled up to the brim. *(2020 C)*

67. (a) Define the following terms :
(i) Enantiomers (ii) Racemic mixture
(b) Why is chlorobenzene resistant to nucleophilic substitution reaction ? *(2019)*

68. (i) Out of $(CH_3)_3C-Br$ and $(CH_3)_3C-I$, which one is more reactive towards S_N1 and why?
(ii) Write the product formed when *p*-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.
(iii) Why *dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation? *(Delhi 2019)*

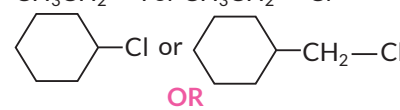
LA (4 marks)

The following questions are case-based questions. Read the case carefully and answer the questions that follow:

69. **Nucleophilic Substitution**

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. S_N1 is a two step reaction while S_N2 is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent.

Influences of solvent polarity : In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction, In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu^- than the transition state, thereby increasing the activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane at 25°C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence, the level of solvent polarity has influence on both S_N1 and S_N2 reaction, but with different results. Generally speaking weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1. Generally speaking the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example ethanol containing water)

Answer the following questions.
(a) Why racemisation occurs in S_N1?
(b) Why is ethanol less polar than water?
(c) Which one of the following in each pair is more reactive towards S_N2 reaction?
(i) CH_3CH_2-I or CH_3CH_2-Cl
(ii)  or

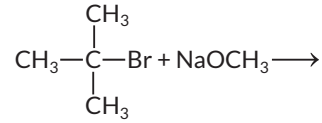
OR

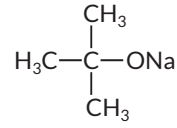
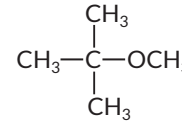
(c) Arrange the following in the increasing order of their reactivity towards S_N1 reactions:
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2 methylbutane, 2-Bromo-3-methylbutane *(2023)*

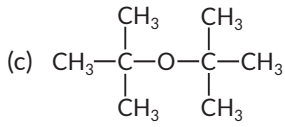
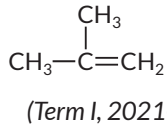
Reaction with Metals, Electrophilic Substitution and Elimination Reactions

MCQ

70. Major product formed in the following reaction



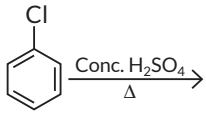
(a)  (b) 

(c)  (d) 

(Term I, 2021-22) An

VSA (1 mark)

71. Write the major product(s) of the following reaction :



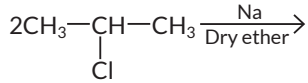
(1/3, 2020)

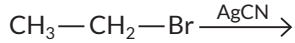
72. Out of 2-bromopentane, 2-bromo-2-methylbutane, and 1-bromopentane, which compound is most reactive towards elimination reaction and why?

(1/3, AI 2019)

SA I (2 marks)

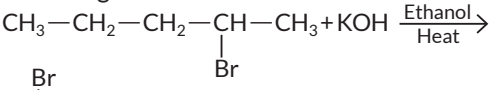
73. Write the major product(s) in the following :

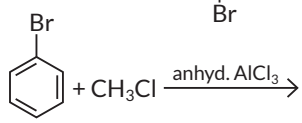
(i) 

(ii) 

(2/3, AI 2016)

74. Write the structure of the major product in each of the following reactions :

(i) 

(ii) 

(2/3, AI 2015)

75. Write chemical equations when

(i) ethyl chloride is treated with aqueous KOH.

(ii) chlorobenzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$. *(Foreign 2014)*

76. Write chemical equations when

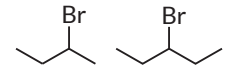
(i) methyl chloride is treated with $AgNO_2$.

(ii) bromobenzene is treated with CH_3Cl in the presence of anhydrous $AlCl_3$. *(Foreign 2014)*

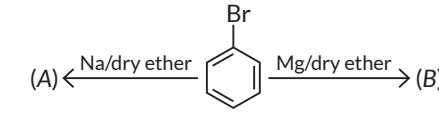
SA II (3 marks)

77. (i) Write the structure of major alkene formed by β-elimination of 2, 2, 3-trimethyl-3-bromopentane with sodium ethoxide in ethanol.

(ii) Which one of the compounds in the following pairs is chiral?

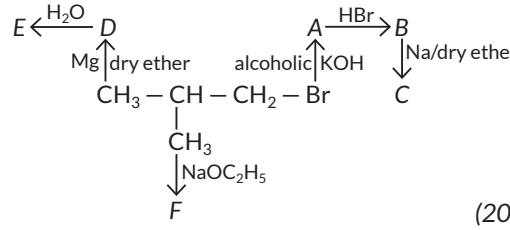


(iii) Identify (*A*) and (*B*) in the following :



(2020) An

78. Identify *A*, *B*, *C*, *D*, *E* and *F* in the following :



(2020) An

79. Among all the isomers of molecular formula C_4H_9Br, identify

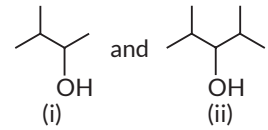
(a) the one isomer which is optically active.

(b) the one isomer which is highly reactive towards S_N2.

(c) the two isomers which give same product on dehydrohalogenation with alcoholic KOH.

(2019)

80. (a) Identify the chiral molecule in the following pair :



(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH. *(2018)*

81. Following compounds are given to you :
2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-elimination reaction. *(Delhi 2017)* U

CBSE Sample Questions

6.4 Methods of Preparation of Haloalkanes

MCQ

1. Major product obtained on reaction of 3-phenylpropene with HBr in presence of organic peroxide is

(a) 3-phenyl-1-bromopropane

(b) 1-phenyl-3-bromopropane

(c) 1-phenyl-2-bromopropane

(d) 3-phenyl -2- bromopropane. *(Term I, 2021-22)*

2. Alkenes decolourise bromine water in presence of CCl_4 due to formation of

(a) allyl bromide (b) vinyl bromide

(c) bromoform (d) vicinal dibromide.

(Term I, 2021-22)

6.5 Preparation of Haloarenes

MCQ

3. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives '*X*' while the reaction of toluene with Cl_2 in presence of light gives '*Y*'. Thus '*X*' and '*Y*' are
   (a) *X* = benzyl chloride, *Y* = *o*- and *p*-chlorotoluene
   (b) *X* = *m*-chlorotoluene, *Y* = *p*-chlorotoluene
   (c) *X* = *o*- and *p*–chlorotoluene, *Y* = trichloromethylbenzene
   (d) *X* = benzyl chloride, *Y* = *m*-chlorotoluene.
   (Term I, 2021-22)

6.6 Physical Properties

MCQ

4. Which of the following isomers has the highest melting point?
   (a) 1,2-Dichlorobenzene
   (b) 1,3-Dichlorobenzene
   (c) 1,4-Dichlorobenzene
   (d) All isomers have same melting points.
   (Term I, 2021-22)

6.7 Chemical Properties

MCQ

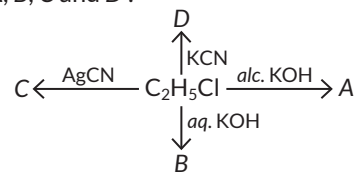
5. Which one of the following compounds is more reactive towards S_N1 reaction?
   (a) $CH_2=CHCH_2Br$
   (b) $C_6H_5CH_2Br$
   (c) $C_6H_5CH(C_6H_5)Br$
   (d) $C_6H_5CH(CH_3)Br$ *(2022-23)*

6. Which of the following is a correct statement for C_2H_5Br?
   (a) It reacts with metallic Na to give ethane.
   (b) It gives nitroethane on heating with aqueous solution of $AgNO_2$.
   (c) It gives C_2H_5OH on boiling with alcoholic potash.
   (d) It forms diethylthioether on heating with alcoholic KSH. *(Term I, 2021-22)*

7. Which reagents are required for one step conversion of chlorobenzene to toluene?
   (a) $CH_3Cl/AlCl_3$
   (b) CH_3Cl, Na, dry ether
   (c) CH_3Cl/Fe dark
   (d) $NaNO_2$/ HCl /0-5°C *(Term I, 2021-22)*

8. Complete the following analogy:
   Same molecular formula but different structures : *A* :: Non superimposable mirror images : *B*
   (a) *A* : Isomers, *B* : Enantiomers
   (b) *A* : Enantiomers, *B* : Racemic mixture
   (c) *A* : Stereoisomers, *B* : Retention
   (d) *A* : Isomers, *B* : Stereoisomers *(2020-21)*

9. Identify *A*, *B*, *C* and *D* :



   (a) $A = C_2H_4, B = C_2H_5OH, C = C_2H_5NC, D = C_2H_5CN$
   (b) $A = C_2H_5OH, B = C_2H_4, C = C_2H_5CN, D = C_2H_5NC$
   (c) $A = C_2H_4, B = C_2H_5OH, C = C_2H_5CN, D = C_2H_5NC$
   (d) $A = C_2H_5OH, B = C_2H_4, C = C_2H_5NC, D = C_2H_5CN$
   (2020-21)

SA I (2 marks)

10. Give reason for the following:
   (a) During the electrophilic substitution reaction of haloarenes, *para*-substituted derivative is the major product.
   (b) The product formed during S_N1 reaction is a racemic mixture.

   OR

   (a) Name the suitable alcohol and reagent, from which 2-chloro-2-methyl propane can be prepared.
   (b) Out of the chloromethane and fluoromethane, which one has higher dipole moment and why?
   (2022-23)

11. The following haloalkanes are hydrolysed in presence of *aq*. KOH :
   (i) 2-Chlorobutane
   (ii) 2-Chloro-2-methylpropane
   Which of the above is most likely to give a racemic mixture? Justify your answer. *(2020-21)*

12. With the help of resonating structures explain the effect of presence of nitro group at *ortho*-position in chlorobenzene.

   OR

   Carry out the following conversions in not more than 2 steps :
   (i) Aniline to chlorobenzene
   (ii) 2-Bromopropane to 1-bromopropane *(2020-21)*

SA II (3 marks)

13. (a) Identify the major product formed when 2-cyclohexylchloroethane undergoes a dehydrohalogenation reaction. Name the reagent which is used to carry out the reaction.
   (b) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes and vinylic halides?

   OR

   (a) Name the possible alkenes which will yield 1-chloro-1-methylcyclohexane on their reaction with HCl. Write the reactions involved.
   (b) Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why? *(2022-23)*

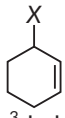
Detailed SOLUTIONS

Previous Years' CBSE Board Questions

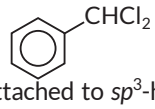
1. **(d) :** Vinyl halide contains C_{sp^2} – *X* bond.

$$\overset{sp^2}{H_2C}=\overset{sp^2}{CH}-Cl$$

Vinyl chloride

2.  is an allylic halide as the halogen is attached to sp^3-hybridised carbon atom which is next to carbon-carbon double bond.

3. is a vinylic halide as the halogen is attached to sp^2-hybridised carbon.

4.  is a benzylic halide as the halide group is attached to sp^3-hybridised carbon atom next to aromatic ring.

Answer Tips

- Benzylic halide : Ph—$\overset{|}{\underset{|}{C}}$—*X*

5. 4-Bromo-4-methylpent-2-ene

6. $Cl-\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_2-Br$

1-Bromo-4-chlorobut-2-ene

7. $H_2C(Br)-C(CH_3)=CH_2$

3-Bromo-2-methylprop-1-ene

8. $H_3C-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

9. (i) $\overset{1}{C}H_2=\overset{2}{C}H\overset{3}{C}H_2Br$

3-Bromoprop-1-ene

(ii) 2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

10. (i) 2-Bromobutane (ii) 1,3-Dibromobenzene
(iii) 3-Chloropropene

11. **(b):** Alkyl chloride or bromide when heated with heavy metal fluoride gives alkyl fluoride in a reaction called Swarts reaction.

$$CH_3-Br + AgF \longrightarrow CH_3-F + AgBr$$

12. **(b) :** *n*-Pentane will give three isomeric monochlorides on photochemical chlorination.

$$CH_3CH_2CH_2CH_2CH_3 \xrightarrow{Cl_2/U.V.\ light} CH_3CH_2CH_2CH_2CH_2Cl + CH_3CH_2CH_2\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 + CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2CH_3$$

13. $CH_3-CH_2-CH=CH_2 + HBr \xrightarrow{Peroxide}$

But-1-ene

$CH_3CH_2CH_2CH_2Br \xrightarrow[NaI]{Acetone} CH_3CH_2CH_2CH_2I$

1-Bromobutane 1-Iodobutane

Key Points

- Follow Anti-Markownikoff's path to get the product.

14. Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO_2 and HCl. These two gaseous products are escapable, hence the reaction gives pure alkyl halides.

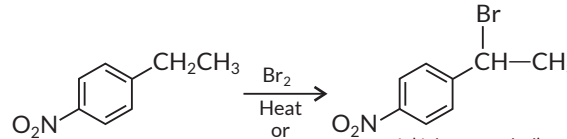
15. Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This is known as Finkelstein reaction.

$$CH_3CH_2CH_2CH_2Cl \xrightarrow[Acetone]{NaI} CH_3CH_2CH_2CH_2I$$

16. $\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{Peroxide} CH_3CH_2CH_2Br$

$\xrightarrow[Acetone]{NaI} CH_3-CH_2-CH_2I$

1-Iodopropane

17. 

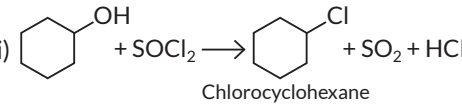
4-(1-bromoethyl) nitrobenzene

Answer Tips

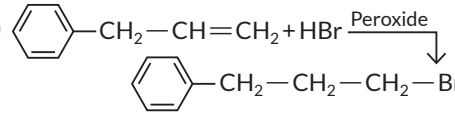
- Side chain halogenation occurs at high temperature in presence of light and in absence of halogen carriers.

18. $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}-CH_3$ (Markownikoff's addition)

2-Bromo-2-methylbutane

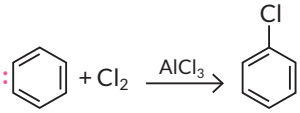
19. (i) 

Chlorocyclohexane

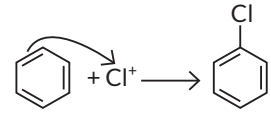
(ii) 

20. $CH_3CH_2\ddot{O}H + H^+ \longrightarrow CH_3CH_2-\overset{+}{\ddot{O}}H_2$

$Br^- + CH_3CH_2-\overset{+}{\ddot{O}}H_2 \longrightarrow CH_3CH_2-Br + H_2O$

21. **(d):** 

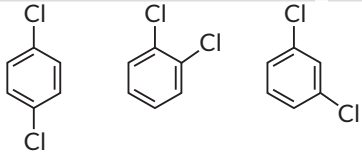
It is an electrophilic substitution reaction. This substitution reaction is initiated by an electrophile Cl^+.



22. **(d):** C_2H_5-I has highest boiling point due to higher molecular mass.

23. (c): For the same alkyl group, the boiling points of alkyl halides decreases in the order :
*R*I > *R*Br > *R*Cl > *R*F. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waals' forces increases.

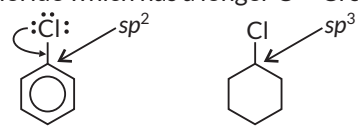
24. *p*-Dichlorobenzene has higher melting point than those of *o*-and *m*-isomers because it is more symmetrical and packing is better in solid form. Hence, it has stronger intermolecular forces of attraction than *o*-and *m*-isomers.



p-isomer *o*-isomer *m*-isomer

25. Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H – bond among water molecules is much higher than energy released by water halide interaction.

26. There are two reasons :
(i) In case of chlorobenzene, carbon to which chlorine is attached is sp^2-hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3-hybridised. So the net dipole moment is lower in chlorobenzene.
(ii) In chlorobenzene, C—Cl bond has some double bond character so its bond length is smaller.
Hence, dipole moment of chlorobenzene is smaller than cyclohexyl chloride which has a longer C—Cl single bond.



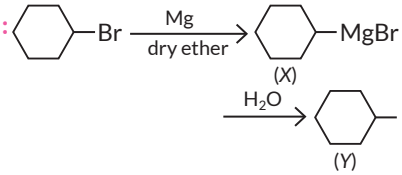
Chlorobenzene Cyclohexyl chloride

27. *n*-Butyl bromide, being a straight chain molecule have strong intermolecular forces whereas *t*-butyl bromide being a branched chain molecule have weaker intermolecular forces due to smaller surface area.
Hence, boiling point of *n*-butyl bromide is higher than that of *t*-butyl bromide.

28. (b): $CH_3-\overset{H}{\underset{CH_2Br}{\overset{|}{\underset{|}{\overset{*}{C}}}}}-Cl$ is marked correctly since it is a chiral carbon with four different groups.

29. (c): The correct order of S_N2 reaction is II > I > III.

30. (c):



31. (b): Enantiomers differ only in rotation of polarised light.

32. (b): Chlorobenzene is less reactive towards nucleophilic substitution reaction due to partial double bond character of C – *X* bond which is very difficult to break.

33. (b): A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether. This reaction is called Wurtz - Fitting reaction.

34. (b): S_N1 reactions are accompanied by racemisation.

35. (b): The conversion of an alkyl halide into an alcohol by aqueous NaOH is a substitution reaction.

36. (d): Order of reactivity towards nucleophilic substitution reaction is alkyl halide > vinyl halide > halobenzene.

37. Stereochemical aspects of nucleophilic substitution reaction in S_N1 proceeds with racemisation.

38. Polarimeter is used for measuring the angle by which the plane polarised light is rotated.

39. $CH_3-CH_2-CH_2-\underset{\text{2-Bromopentane}}{\overset{Br}{\overset{|}{CH}}}-CH_3 + KOH_{(alc.)} \longrightarrow$

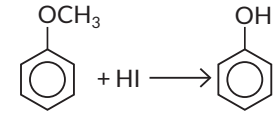
$CH_3-CH_2-\underset{\text{Pent-2-ene (Major)}}{CH=CH}-CH_3 +$ $\underset{\text{Pent-1-ene (Minor)}}{CH_3-CH_2-CH_2-CH=CH_2}$

Answer Tips

- Apply Saytzeff's rule.
- More substituted alkene will be more stable.

40. Iodoform (CHI_3) is used as a mild antiseptic.

41.

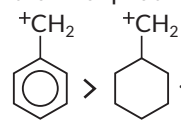


Anisole Phenol

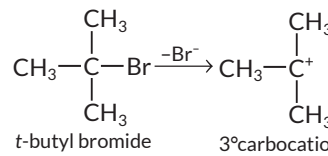
Commonly Made Mistake

- Remember cleavage of phenolic ethers always gives the phenol and the corresponding alkyl halide.

42. $-CH_2Cl$ will react faster in S_N1 reaction since benzyl carbocation is more stable carbocation than aliphatic primary cyclohexyl carbocation, *i.e.*,



43. The S_N1 reaction proceeds through carbocation formation. Thus, the compound which forms more stable carbocation, will be more reactive.



t-butyl bromide 3°carbocation (More stable)

$CH_3-CH_2-CH_2-CH_2-Br \xrightarrow{-Br^-} CH_3-CH_2-CH_2-\overset{+}{C}H_2$

1°carbocation (Less stable)

Therefore, *t*-butyl bromide is more reactive towards S_N1 reaction as compared to *n*-butyl bromide.

44. Cyclohexyl chloride is more reactive than chlorobenzene towards nucleophilic substitution reaction as it forms a stable 2° carbocation. Aryl halides are extremely

less reactive towards nucleophilic substitution reaction. In aryl halides due to reasonance, C – *X* bond acquires a partial double bond character, hence C – *X* bond cleavage is difficult. Also in aryl halide, the carbon atom attached to halogen is sp^2 hybridised, hence the electron pair of C – *X* bond is more tightly held.

45. 2° alkyl halide *i.e.*, $CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{CH}}}}-Br$ would undergo S_N2 reaction faster than compared to 3° alkyl halide *i.e.*, $(CH_3)_3CBr$ due to formation of less sterically hindered transition state.

46. Benzyl chloride gets easily hydrolysed by *aq*. NaOH due to formation of stable benzyl carbocation. But due to partial double bond character of C — Cl bond in chlorobenzene, it does not hydrolyse.

47. The S_N1 reaction proceeds through carbocation formation thus, the compound which forms more stable carbocation will be more reactive.

$$\underset{\text{2-Chlorobutane}}{CH_3-CH_2-\underset{CH_3}{\overset{|}{CH}}-Cl} \xrightarrow{-Cl^-} \underset{\text{(2° Carbocation)}}{CH_3-CH_2-\overset{+}{\underset{CH_3}{\overset{|}{CH}}}}$$

2° carbocation will undergo faster reaction.

48. $\underset{\text{tert-butyl bromide}}{CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-Br}$ is an isomer of C_4H_9Br that undergoes S_N1 reaction faster due to formation of 3° carbocation.

Answer Tips

➲ It forms 3° carbocation which is most stable.

49. $CH_3—CH_2—Br$ would undergo S_N2 reaction faster due to formation of less sterically hindered transition state.

50. $CH_3-\underset{Br}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$ will undergo S_N1 reaction faster due to the formation of stable 3° carbocation.

51. Since, I^- is a better leaving group than Br^-, thus, CH_3CH_2I undergoes S_N2 reaction faster than CH_3CH_2Br.

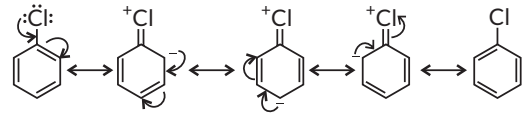
52. is a chiral molecule.

53. (i) CH_3I will give faster S_N2 reaction.
(ii) CH_3Cl will give faster S_N2 reaction.

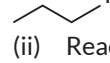
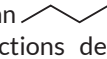
54. (a) $CH_3-\underset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{PCl_5} \underset{(A)}{CH_3-\underset{Cl}{\overset{|}{CH}}-CH_3} \xrightarrow{AgCN} \underset{(B)}{CH_3-\underset{NC}{\overset{|}{CH}}-CH_3}$

(b) $CH_3CH_2CH_2Cl + KOH \xrightarrow{\text{Ethanol}} \underset{(A)}{CH_3-CH=CH_2} \xrightarrow{HBr} \underset{(B)}{CH_3-\underset{Br}{\overset{|}{CH}}-CH_3}$

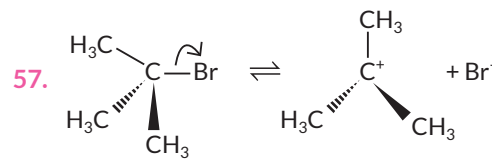
55. Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
(i) Resonance effect : In haloarenes the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.

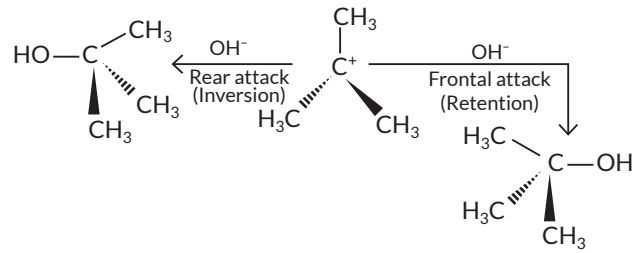


C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, haloarenes are less reactive towards nucleophilic substitution reaction.
(ii) In haloarenes, halogen is attached to sp^2-hybridised carbon while in haloalkanes, halogen is attached to sp^3-hybridised carbon.

56. (i) Since, I^- is a better leaving group than Cl^-, therefore  will react faster than  in S_N2 reactions.
(ii) Reactivity in S_N2 reactions depends upon steric hindrance. Since, 1° alkyl halides experience less steric hindrance than 3° alkyl halides, therefore $CH_3—CH_2Cl$ will react faster than $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-Cl$.

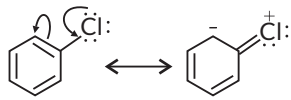
57.



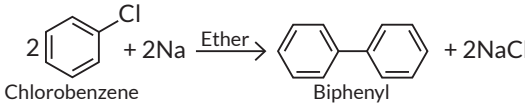


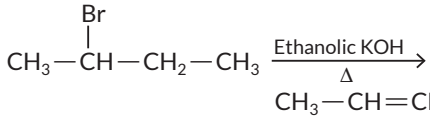
58. (i) Racemic mixture contains equal amount of *d*- and *l*-forms, hence rotation due to one enantiomer is cancelled by another.
(ii) The presence of nitro group at *o*-and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

59. (i) In halobenzene, C—*X* bond has partial double bond character due to resonance while CH_3—*X* bond is single bond.
Thus, bond length of C—*X* bond in halobenzene is smaller than that in CH_3—*X*.

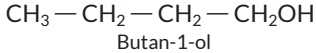


(ii) In S_N1 reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and an equimolar mixture of two components are formed and resulting mixture is optically inactive.

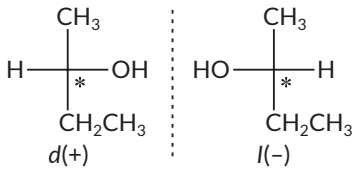
60. (i) 
Chlorobenzene — Biphenyl

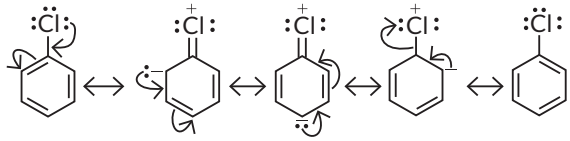
(ii) 

61. (i) Butan-1-ol is achiral, *i.e.*, does not have chiral 'C' atom which is attached to four different groups, therefore, it is optically inactive.

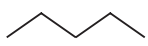

Butan-1-ol
(Optically inactive)
(No chiral carbon)

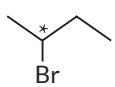
Butan-2-ol is chiral, *i.e.*, it has chiral 'C' atom, attached to four different groups.


d(+) Butan-2-ol — *l*(−) Butan-2-ol

(ii) 

Although, Cl is electron withdrawing group (*-I* effect) but still it is *o*- and *p*-directing as due to *+R* effect, electron density is maximum at *o*- and *p*-positions.

62. (i) (a)  Br undergoes faster S_N2 reaction.

(b)  is chiral.

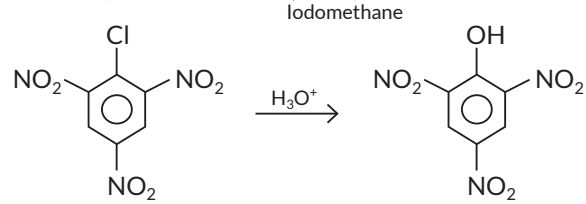
(ii) (a) S_N2 reaction occurs with inversion of configuration.
(b) S_N1 reaction occurs with racemisation.

63. (i) 1-Bromobutane is 1° alkyl halide while 2-bromobutane is 2° alkyl halide. Due to steric hindrance in 2° alkyl halides, 1° alkyl halide will react faster than 2° alkyl halide in S_N2 reaction.

(ii) In S_N1 reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and a equimolar mixture of two components are formed and resulting mixture is optically inactive.

64. A nucleophile which can attack from more than one centres, is known as ambident nucleophile,
e.g., $^-\ddot{C}\equiv N:$, cyanide ion.
$R-X + AgCN \longrightarrow R-NC + AgX$; $R-X + KCN \longrightarrow R-CN + KX$

65. (a) $CH_3Cl + NaI \xrightarrow{\text{Acetone}} \underset{\text{Iodomethane}}{CH_3I} + NaCl$

(b) 
Picric acid

(c) $H_3C-CH_2-CH_2-CH_2-Cl \xrightarrow{\text{alc. KOH}} \underset{\text{But-1-ene}}{H_3C-CH_2-CH=CH_2}$

66. (a) Grignard reagents react with water to form alkanes.

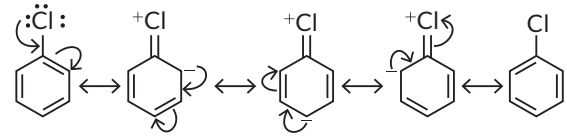
$$R-Mg-X + H_2O \longrightarrow R-H + Mg\begin{matrix}X\\OH\end{matrix}$$

So, they must be prepared under anhydrous conditions.
(b) Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H – bond among water molecules is much higher than energy released by water halide interaction.
(c) Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

$$CHCl_3 + \frac{1}{2}O_2 \rightarrow \underset{\text{Phosgene}}{COCl_2} + HCl$$

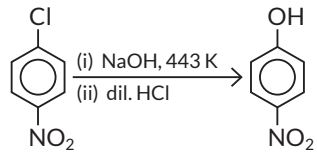
Thus, it is kept in dark coloured bottles to prevent the oxidation.

67. (a) (i) The stereoisomers related to each other as non-superimposable mirror images are called enantiomers.
(ii) A mixture containing two enantiomers in equal proportions will have zero optical rotation as the rotation due to one isomer will be cancelled by the rotation due to other isomer. Such a mixture is known as racemic mixture.
(b) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.
(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.
(ii) In halorenes, halogen is attached to sp^2-hybridised carbon while in haloalkanes, halogen is attached to sp^3-hybridised carbon.

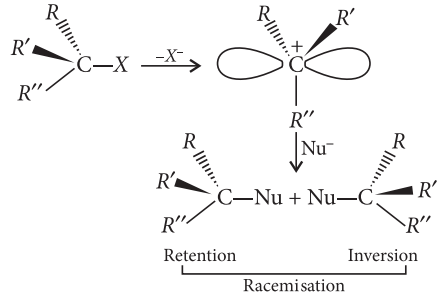
68. (i) $(CH_3)_3C-I$ is more reactive because C—I bond has the minimum bond dissociation enthalpy.

(ii) 

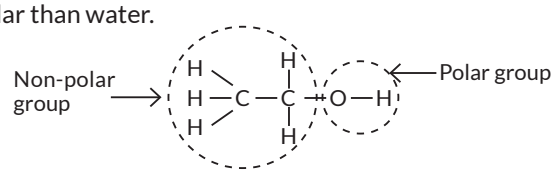
4-Nitrophenol

(iii) *Dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation because they have almost same boiling point.

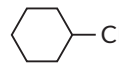
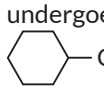
69. (a) Carbonium ion intermediate produced in the course of S_N1 reaction has a planar structure. It can be attacked by the nucleophilic reagent from either side to give two isomers *d* and *l* if the starting alkyl halide is asymmetric.
Thus, a racemic mixture is obtained due to formation of equal amount of *d* and *l* forms and optical activity is lost.



(b) In water, two hydrogen atoms are attached to one oxygen atom. The bonds are attached in such a way that the dipoles of oxygen –hydrogen bonds add constructively. Due to the difference in electronegativity of oxygen and hydrogen, water molecule is much more polar.
In ethanol, one of the hydrogen atom is replaced by a hydrocarbon group which is non-polar in nature. Due to the low polarity of the hydrocarbon group, ethanol is less polar than water.



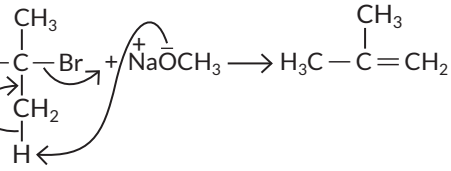
(c) (i) As iodide is a better leaving group than chloride because of its large size, therefore, CH_3CH_2I undergoes S_N2 reaction faster than CH_3CH_2Cl.

(ii)  is a primary halide and therefore, undergoes S_N2 reaction faster than the secondary halide  .

OR

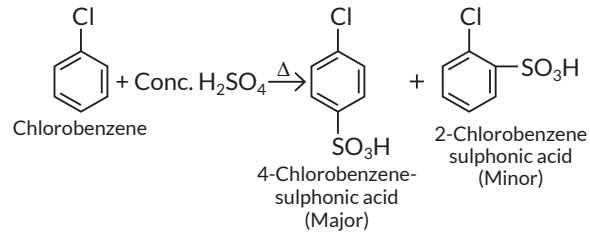
(c) (i) The reactivity order toward S_N1 is 2-bromo-2-methylbutene > 2-bromopentane > 1-bromopentane as the reactivity of S_N1 reaction is 3° > 2° > 1°.

(ii) The reactivity order is 2-bromo-2-methylbutane > 2-bromo-3-methylbutane > 1-bromo-3-methylbutane as the stability order of carbocation and reactivity order of S_N1 reaction is 3° > 2° > 1°.

70. (d): 

Concept Applied

➲ With strong bases like $CH_3CH_2O^-$, *t*-butyl bromide undergoes elimination rather than substitution.

71. 

Chlorobenzene
4-Chlorobenzene-sulphonic acid (Major)
2-Chlorobenzene sulphonic acid (Minor)

72. 2-Bromo-2-methylbutane will give fastest elimination reaction because it is a *tert*-halide and *tert*-halides prefer elimination reaction.

73. (i) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ (ii) CH_3CH_2NC

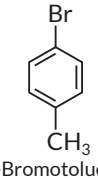
Commonly Made Mistake

➲ Remember, Alkyl halide —(*Alc.* KCN)→ Alkyl cyanide; —(*Alc.* AgCN)→ Alkyl isocyanide

74. (i) $CH_3-CH_2-CH=CH-CH_3$ (Saytzeff rule)
Pent-2-ene

Commonly Made Mistake

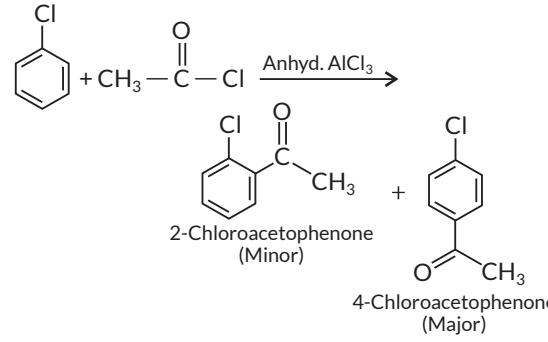
➲ Remember, Alkyl halide —(*aq.* KOH)→ Alcohol; —(*alc.* KOH)→ Alkene

(ii) 

4-Bromotoluene (Friedel—Crafts alkylation)

75. (i) When ethyl chloride is treated with aqueous KOH, ethanol is formed,

$CH_3CH_2Cl + KOH_{(aq)} \longrightarrow CH_3CH_2OH + KCl$

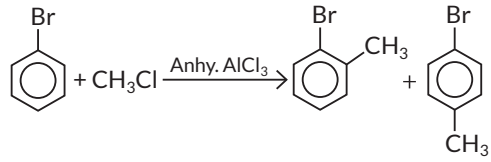
(ii) 

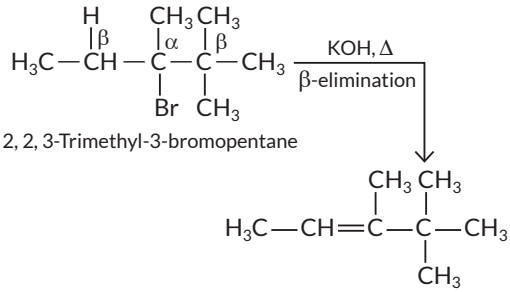
2-Chloroacetophenone (Minor)
4-Chloroacetophenone (Major)

76. (i) $CH_3Cl + AgNO_2 \longrightarrow CH_3NO_2 + AgCl$

Commonly Made Mistake

➲ Remember, Alkyl halide —(KNO_2)→ Alkyl nitrite; —($AgNO_2$)→ Nitroalkane

(ii) 

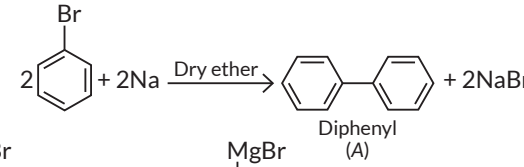
77. (i) 

2, 2, 3-Trimethyl-3-bromopentane

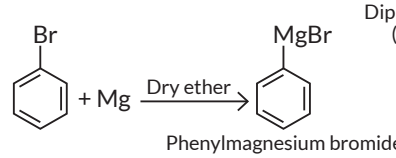
Answer Tips

➲ H is available only on one β-carbon only one product will be formed.

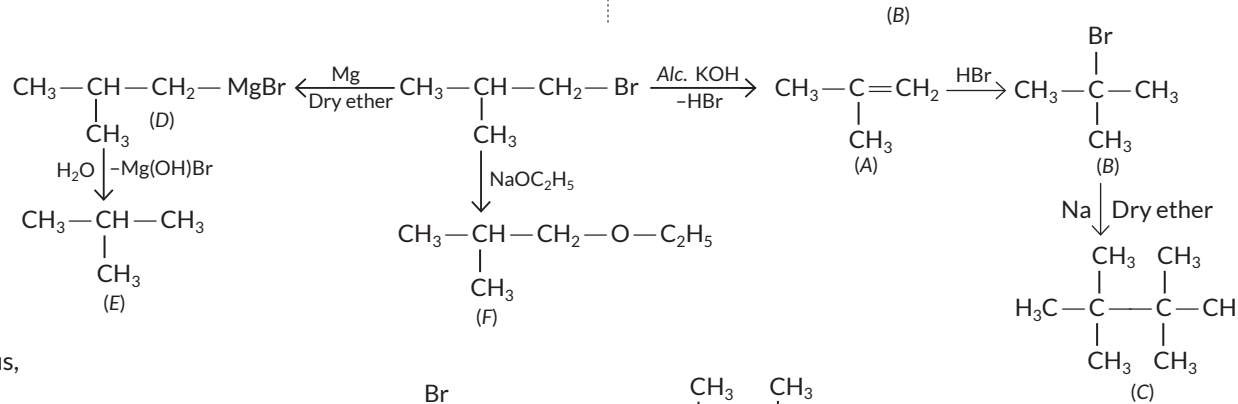
(ii)

(iii) 

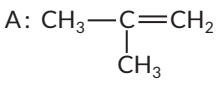
Diphenyl (*A*)

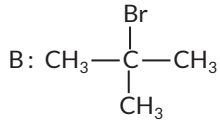


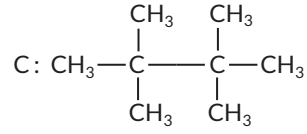
Phenylmagnesium bromide (*B*)

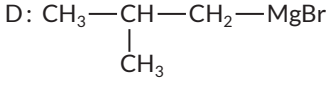
78. 

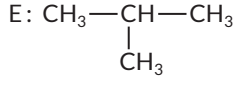
Thus,

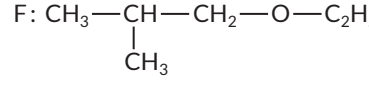
A: 

B: 

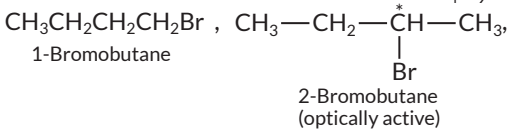
C: 

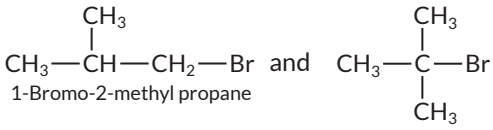
D: 

E: 

F: 

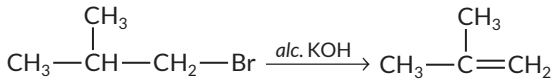
79. The isomers of molecular formula C_4H_9Br are



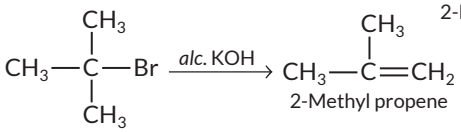


(a) 2-Bromopropane is optically active.

(b) 1-Bromobutane is highly reactive towards S_N2 reaction as 1° alkyl halides are less sterically hindered.

(c) 

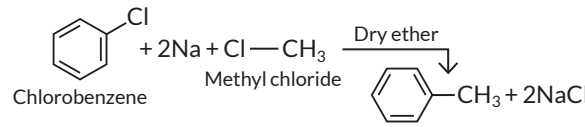
2-Methyl propene



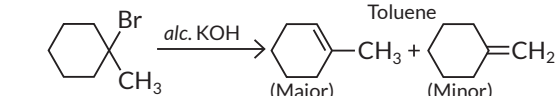
2-Methyl propene

80. (a)

is a chiral molecule.
(i)

(b) 

Chlorobenzene — Methyl chloride — Toluene

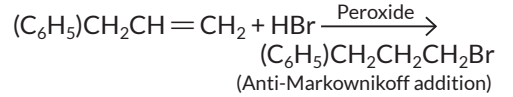
(c) 

1-Bromo-1-methylcyclohexane — (Major) — (Minor)

81. (i) 1-Bromopentane (ii) 2-Bromopentane
(iii) 2-Bromo-2-methylbutane

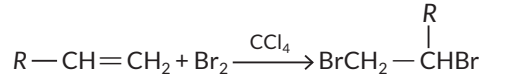
CBSE Sample Questions

1. **(b):** 1-Phenyl-3-bromopropane is formed.



(Anti-Markownikoff addition) **(0.77)**

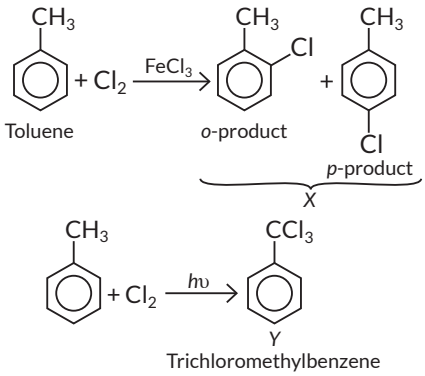
2. **(d):** Vicinal dibromide is formed.



(0.77)

3. **(c):** The reaction of toluene with Cl_2 in presence of $FeCl_3$ is electrophilic substitution reaction forming

o-chlorotoluene and *p*-chlorotoluene. Reaction taking place in the presence of light gives '*Y*', *via* free radical mechanism forming trichloromethylbenzene.



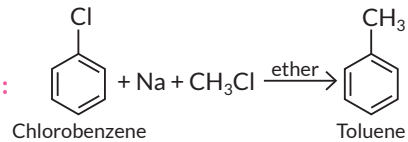
Thus '*X*' and '*Y*' are, *X* = *ortho* and *para*-chlorotoluene, *Y* = trichloromethylbenzene. **(0.77)**

4. (c): 1,4-Dichlorobenzene has higher melting point because *para* isomers are more symmetric than *ortho* and *meta* isomers. **(0.77)**

5. (c): $[C_6H_5CH(C_6H_5)Br] \longrightarrow [C_6H_5\overset{+}{C}H(C_6H_5)]$
Here, carbocation formed is more stable through resonance with two benzene ring. **(1)**

6. (b) : C_2H_5Br gives nitroethane on heating with aqueous solution of $AgNO_2$. C_2H_5Br reacts with metallic Na to give butane · C_2H_5Br gives ethene on boiling with alcoholic potash and forms C_2H_5SH (thiol) on heating with alcoholic KSH. **(0.77)**

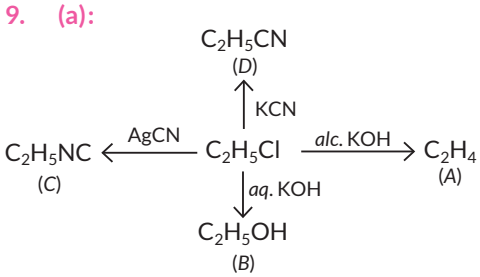
7. (b):



This is also called Wurtz–Fittig reaction. **(0.77)**

8. (a): A : Isomers, B : Enantiomer
Isomers have same molecular formula but different structure and enantiomers are non-superimposable mirror images. **(1)**

9. (a):



(1)

10. (a) At the *ortho* position, higher steric hindrance is present, hence *para* isomer is usually predominant and is obtained in the major amount. **(1)**
(b) During the S_N1 mechanism, intermediate carbocation formed is sp^2 hybridized and planar in nature. This allows the attack of nucleophile from either side of the plane resulting in a racemic mixture. **(1)**

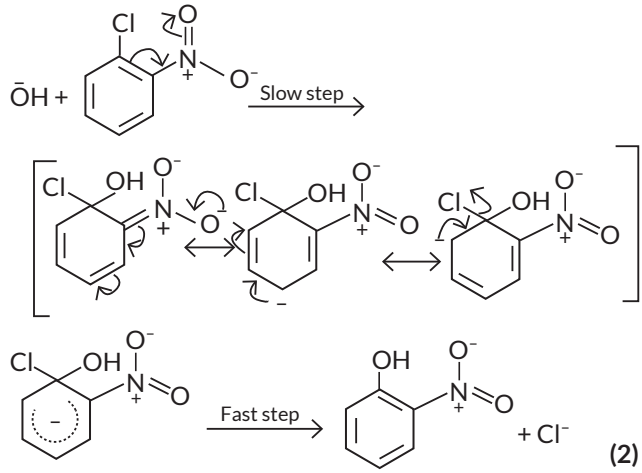
OR

(a) *tert*-Butyl alcohol or 2-methyl propan-2-ol reacts with Lucas reagent (mixture of conc. HCl and $ZnCl_2$) to form 2-chloro-2-methylpropane through S_N1 mechanism. **(1)**

(b) Chloromethane have higher dipole moment and due to smaller size of fluorine, the dipole moment of flouromethane is comparatively lesser. **(1)**

11. Racemic mixture will be given by 2-chlorobutane as it is an optically active compound. **(1)**
When 2-chlorobutane undergoes S_N1 reaction, both front and rear attack are possible, resulting in a racemic mixture. **(1)**

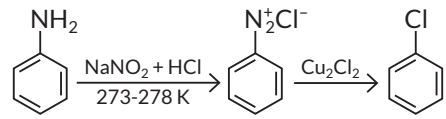
12. Nitro group at *ortho* position withdraws the electron density from benzene ring and thus facilitates the attack of the nucleophile on haloarene.



(2)

OR

(i)



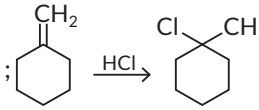
(1)

(ii) $CH_3CH(Br)CH_3 \xrightarrow{alc.\ KOH} CH_3CH{=}CH_2$
$\xrightarrow{HBr,\ organic\ peroxide} CH_3CH_2CH_2Br$ **(1)**

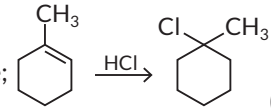
13. (a) The major product formed when 2-cyclohexyl-chloroethane undergoes dehydrohalogenation reaction is 1-cyclohexylethene. The reagent which is used to carry out the reaction is ethanolic KOH. **(2)**
(b) Haloalkanes are more reactive than haloarenes and vinylic halides because of the presence of partial double bond character of C-*X* bond in haloarenes and vinylic halides. Hence, they do not undergo nucleophilic reactions easily. **(1)**

OR

(a) (i) Methylenecyclohexane ;



(ii) 1-Methylcyclohexene;



(2)

(b) Allyl chloride shows high reactivity as the carbocation formed in the first step is stabilised by resonance while no such stabilisation of carbocation exists in the case of *n*-propyl chloride. **(1)**

Self Assessment

Case Based Questions (5 marks)

1. **Read the passage given below and answer the following questions :**

Haloarenes are less reactive than haloalkanes. The low reactivity of haloarenes can be attributed to

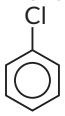
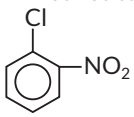
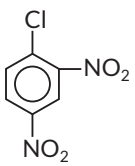
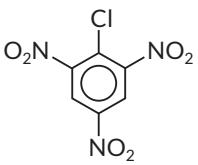
- resonance effect
- sp^2 hybridisation of carbon
- polarity of C — *X* bond
- instability of phenyl cation (formed by self-ionisation of haloarene)
- repulsion between the electron rich attacking nucleophiles and electron rich arenes.

Reactivity of haloarenes can be increased or decreased by the presence of certain groups at certain positions for example, nitro ($-NO_2$) group at *o*/*p*-positions increases the reactivity of haloarenes towards nucleophilc substitution reactions.

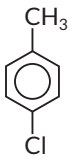
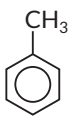
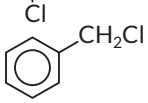
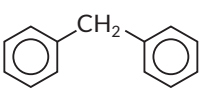
(i) Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to

(a) the formation of more stable carbonium ion
(b) resonance effect
(c) larger carbon-halogen bond
(d) inductive effect.

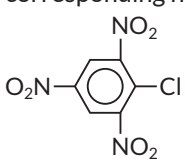
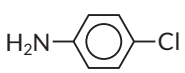
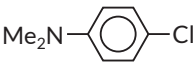
(ii) Which of the following aryl halides is the most reactive towards nucleophilic substitution?

(a) 
(b) 
(c) 
(d) 

(iii) Which one of the following will react fastest with aqueous NaOH?

(a) 
(b) 
(c) 
(d) 

(iv) Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

(a) 
(b) 
(c) 
(d) C_6H_5Cl

(v) The reactivity of the compounds (i) MeBr, (ii) $PhCH_2Br$, (iii) MeCl, (iv) *p*-$MeOC_6H_4Br$ decreases as

(a) (i) > (ii) >(iii) > (iv)
(b) (iv) > (ii) >(i) > (iii)
(c) (iv) > (iii) >(i) > (ii)
(d) (ii) > (i) >(iii) > (iv)

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

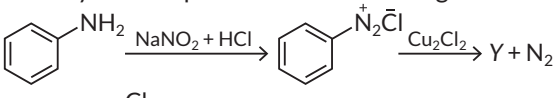
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

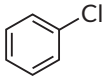
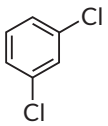
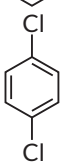
2. **Assertion :** Chlorobenzene is more reactive than benzene towards the electrophilic substitution reaction.
Reason : Due to resonance, the electron density increases more at *ortho* and *para* than at *meta* positions.

3. **Assertion :** 1, 2-dichloroethane is optically active.
Reason : Meso compound is optically inactive.

Multiple Choice Questions (1 mark)

4. Identify the compound *Y* in the following reaction.



(a) 
(b)
(c) 
(d) 

OR

Elimination reaction of 2-bromopentane to form pent-2-ene

(A) is β-Elimination reaction
(B) follows Saytzeff's rule
(C) is dehydrohalogenation reaction
(D) is dehydration reaction.

The correct statements are

(a) (A), (B), (C)
(b) (A), (C), (D)
(c) (B), (C), (D)
(d) (A), (B), (D)

5. Which reagent will you use for the following reaction?

$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

(a) Cl_2/UV light

(b) $NaCl + H_2SO_4$ (c) Cl_2 gas in dark
(d) Cl_2 gas in the presence of iron in dark

6. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?
(a) Cl^- (b) Cl^+ (c) $AlCl_3$ (d) $[AlCl_4]^-$

VSA Type Questions (1 mark)

7. What is an ambident nucleophile?
8. What is the order of reactivity of 1°, 2° and 3° alkyl halides towards S_N2 reaction?
9. Define the term racemisation.
10. Under what condition 2-methyl propene can be converted into *iso*-butyl bromide?
11. What is Fittig reaction?

SA I Type Questions (2 marks)

12. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.
13. (i) Predict the order of reactivity of the following compounds in S_N1 reaction.
$C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$
(ii) Give a chemical test to distinguish between C_2H_5Br and C_6H_5Br.
14. Reactions of arene with iodine is carried out in the presence of an oxidising agent. Why?
15. The boiling point of alkyl halides are higher than those of the hydrocarbons of comparable molecular mass. Explain.
16. (i) Write the isomers of C_3H_5Br having
(a) Br at vinylic position
(b) Br at allylic position.
(ii) What is the advantage of using $SOCl_2$ in the preparation of *R* — Cl from alcohol?

OR

State Saytzeff rule with example.

SA II Type Questions (3 marks)

17. (a) What are nucleophilic substitution reactions?
(b) Explain why 3° alkyl halides undergo S_N1 reaction very fast.
18. (a) What is Wurtz reaction?
(b) What happens when Grignard reagent reacts with a source of proton?
19. (a) What is Grignard's reagent? How is it prepared?
(b) In the preparation of Grignard's reagent all the starting materials must be dry. Why?
20. Name the alkene which will yield 1-chloro-1-methyl -cyclohexane by its reaction with HCl. Write the reactions involved.

OR

How can you obtain iodoethane from ethanol when no other iodine containing reagent except NaI is available in the laboratory?

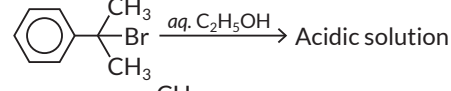
Case Based Questions (4 marks)

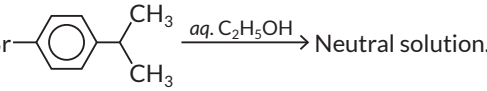
21. **Read the passage given below and answer the following questions :**
The substitution reaction of alkyl halide mainly occurs by S_N1 or S_N2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S_N1 reactions are governed by the stability of carbocation whereas for S_N2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.
(a) Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S_N1 mechanism.
(b) Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?
(c) What are the points of similarities between S_N1 and S_N2 reactions?

OR

Following compounds are given to you :
2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane
(i) Write the compound which is most reactive towards S_N2 reaction.
(ii) Write the compound which is optically active.

LA Type Questions (5 marks)

22. Give reasons for the following :
(a) I. Write a chemical test to distinguish between :
(i) Chlorobenzene and benzyl chloride
(ii) Chloroform and carbon tetrachloride
II. Why is methyl chloride hydrolysed more easily than chlorobenzene?
(b) Explain :
(i) 

(ii) 

23. (a) Haloalkanes easily dissolve in organic solvents, why?
(b) Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment?
(c) Explain the given trend of the boiling point of the following :
MeI > MeBr > MeCl > MeF > CH_4

24. When bromobenzene is monochlorinated, two isomeric compounds (*A*) and (*B*) are obtained. Monobromination of (*A*) gives several isomeric products of formula $C_6H_3ClBr_2$ while monobromination of (*B*) yields only two isomers (*C*) and (*D*). Compound (*C*) is identical with one of the compounds obtained from the bromination of (*A*), however (*D*) is totally different from any of the isomeric compounds obtained from bromination of (*A*). Give structures of (*A*), (*B*), (*C*) and (*D*) and also suggest structures of four isomeric monobrominated products of (*A*).

25. (i) Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why?

(ii) Write a test to detect the presence of double bond in a molecule.

(iii) Out of the various possible isomers of C_7H_7Cl containing benzene ring, suggest the structure with the weakest C — Cl bond.

OR

(i) Predict the major product formed when HCl is added to *iso*-butylene. Explain the mechanism involved.

(ii) Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium? Give reason for your answer.

(iii) Why are alkyl halides generally not prepared in the laboratory by free radical halogenation of alkanes?

Detailed SOLUTIONS

1. **(i) (b)**

(ii) (d): When in aryl halides the electron withdrawing groups are attached at *ortho* and *para*-positions, then the reactivity towards nucleophillic substitution reaction increase. 2,4,6-trinitrochlorobenzene is the most reactive among given aryl halides.

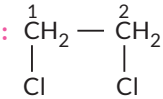
(iii) (d): It will give most stable carbocation.

(iv) (a): —Cl in 2,4,6-trinitrochlorobenzene is activated by three $-NO_2$ groups at *o* and *p*-positions and hence undergoes hydrolysis most readily.

(v) (d): The order of reactivity follows the sequence:
benzyl halides > alkyl halides > aryl halides.
Out of chlorides and bromides, bromides are more reactive.
Therefore, the correct order of reactivity is
(ii) $PhCH_2Br$ > (i) MeBr > (iii) MeCl > (iv) p-$MeOC_6H_4Br$

2. **(d):** Chlorobenzene is less reactive than benzene towards the electrophilic substitution reactions due to $-I$-effect.

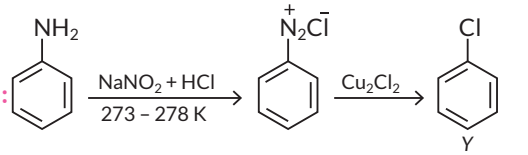
3. **(d):**



1, 2 - dichloroethane

Since, it has no chiral carbon, it is optically inactive. Meso compounds are optically inactive.

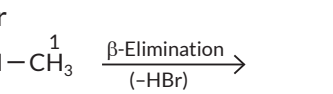
4. **(a):**



Chlorobenzene

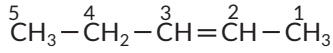
OR

(a):



2-Bromopentane

dehydrobromination



Pent-2-ene
(More substituted alkene is formed, Saytzeff's rule)

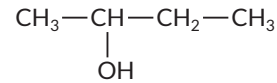
5. **(a):** Direct chlorination of alkanes takes place in presence of sunlight (UV light).

6. **(b):** Cl^+ is an electrophile formed by the following reaction. $AlCl_3 + Cl_2 \longrightarrow AlCl_4^- + Cl^+$
Cl^+ attacks the benzene ring to give chlorobenzene.

7. Molecules or ions having two nucleophilic centres are called ambident nucleophiles, *e.g.* CN^- ion.

8. Order of reactivity towards S_N2 reaction :
1° > 2° > 3° alkyl halide

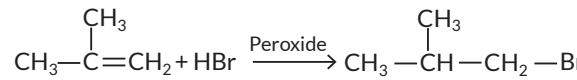
9. The equimolar mixture of *d*-form and *l*-form, which is optically inactive is known as racemic mixture and the process of its formation is called racemisation.



(±) Butan-2-ol

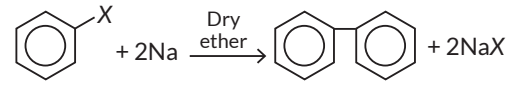
(±) Butan-2-ol contains equal amounts of the two enantiomers *i.e.*, (+) butan-2-ol and (–) butan-2-ol. Thus, it is a racemic mixture.

10.



2-methyl propene — Isobutyl bromide

11. **Fittig reaction :** Aryl halide on reaction with sodium in the presence of dry ether gives diaryl.



Diphenyl

12. In haloarenes, –ve charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution.
Haloalkanes have electrophilic carbon centre due to polarity of C→X bond.

13. (i) $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

(ii) C_2H_5Br reacts with $AgNO_3$ to give yellow precipitate of AgBr while C_6H_5Br will not.

14. Reactions of arene with iodine are reversible in nature and require the presence of an oxidising agent to oxidise the HI formed during the reaction and shift the reaction towards right.

15. Molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole interaction and van der Waals' forces) are stronger and hence have higher boiling point than hydrocarbons of comparable molecular masses.

16. (i) (a) Br at vinylic position : $CH_3CH=CHBr$;

$$CH_3C(Br)=CH_2$$

(b) Br at allylic position : $CH_2=CHCH_2Br$

(ii) $R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$

SO_2 and HCl in the gaseous form escape from the reaction mixture hence, $R-Cl$ is isolated in pure form.

OR

Saytzeff rule states "In dehydrohalogenation reactions, the preferred product is that alkene which has greater number of alkyl groups attached to the double bonded carbon atoms."

$$CH_3-CH_2-CH_2-\underset{Br}{CH}-CH_3 \xrightarrow{alc.\ KOH} \underset{\text{Pent-2-ene}}{CH_3-CH_2-CH=CH-CH_3}$$

17. (a) Those substitution reactions which are initiated by a nucleophile are called nucleophilic substitution reactions.

$$>C^{+\delta}-X^{-\delta} + Nu^- \longrightarrow >C-Nu + X^-$$

(b) In S_N1 reaction, carbocation intermediate is formed. 3° carbocation is most stable. So, 3° alkyl halides undergo S_N1 reaction very fast.

18. (a) Alkyl halides react with sodium in presence of dry ether to give higher hydrocarbons. This reaction is called Wurtz reaction.

$$2RX + 2Na \xrightarrow{\text{Dry ether}} R-R + 2NaX$$

(b) Grignard reagent reacts with a source of proton to give hydrocarbon.

$$RMgX + \overset{+}{H}\overset{-}{A} \longrightarrow RH + Mg(A)X$$

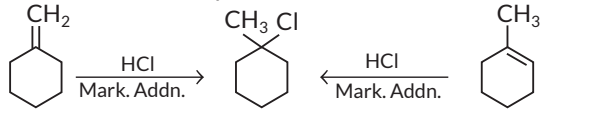
19. (a) Alkyl or aryl magnesium halide is called Grignard reagent. It is prepared by refluxing alkyl halide with Mg in dry ether.

$$R-X + Mg \xrightarrow{\text{Dry ether}} RMgX$$

(b) If any starting material contains moisture then Grignard reagent is converted into alkane.

$RMgX + H_2O \rightarrow RH + Mg(OH)X$

20. Two alkenes are possible. These are :



Methylene-cyclohexane — 1-Chloro-1-methylcyclohexane — 1-Methylcyclohex-1-ene

OR

First convert ethanol to chloroethane on treatment with $HCl_{(g)}$ and anhyd. $ZnCl_2$ (or bromoethane on treatment with $P + Br_2$) and then to iodoethane on treatment with NaI in acetone by Finkelstein reaction.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + HCl \xrightarrow{\text{Anhyd. } ZnCl_2} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + H_2O$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\text{Red P + } Br_2} \underset{\text{Bromoethane}}{CH_3CH_2Br}$$

$$\underset{\text{Chloroethane}}{CH_3CH_2Cl} \text{ or } \underset{\text{Bromoethane}}{CH_3CH_2Br} + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{Acetone}} \underset{\text{Iodoethane}}{CH_3CH_2I} + NaCl \text{ or } NaBr$$

21. (a) Stereochemical aspects of nucleophilic substitution reaction in S_N1 proceeds with racemisation.

(b) Benzyl chloride gets easily hydrolysed by *aq.* NaOH due to formation of stable benzyl carbocation. But due to partial double bond character of C—Cl bond in chlorobenzene, it does not hydrolyse.

(c) Both S_N1 and S_N2 reactions undergo substitution of a nucleophile by other nucleophile. In both the reactions configuration of product changes, partially in S_N1 and completely in S_N2.

OR

(i) 1-Bromopentane (ii) 2-Bromopentane

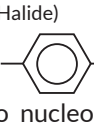
22. (a) I. (i) Benzyl chloride gives white precipiate with $AgNO_3$ solution while chlorobenzene does not.

(ii) $CHCl_3$ with aniline in presence of *alc.* KOH gives foul smelling isocyanides whereas CCl_4 does not.

II. CH_3Cl is hydrolysed easily than C_6H_5Cl as chlorobenzene has partial double bond character between C—Cl bond which is difficult to break.

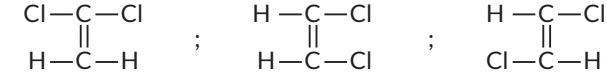
(b) (i) It is a 3° halide so it undergoes S_N1 reaction forming HBr as one of the products. Due to HBr, the solution becomes acidic.

$$\underset{\text{(3° Halide)}}{C_6H_5-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br} \xrightarrow{C_2H_5OH(aq)} \underset{\text{(Makes solution acidic)}}{C_6H_5-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OC_2H_5} + HBr$$

(ii)  $CH(CH_3)_2$ is an aryl halide so it does not undergo nucleophilic substitution reactions. Hence, its solution will remain neutral.

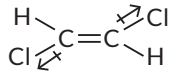
23. (a) Haloalkanes dissolve in organic solvents because the intermolecular attractions between haloalkanes and organic solvent molecules have the same strength as in the separate haloalkanes and solvent molecules.

(b) Dichloroethene exists in following three isomeric forms :



1, 1-Dichloroethene ; *cis*-1, 2-Dichloroethene ; *trans*-1, 2-Dichloroethene

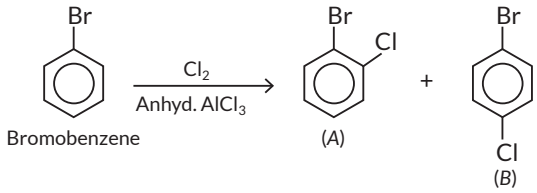
The resultant dipole moment will be zero in case of *trans*-1, 2-dichloroethene.



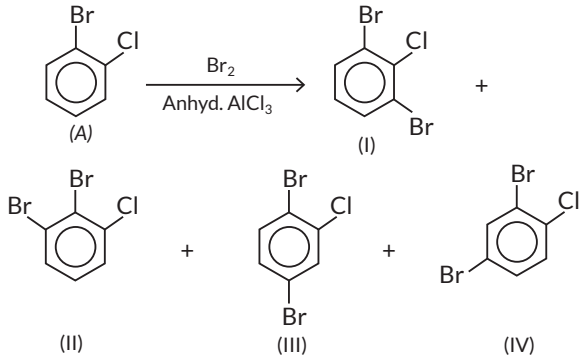
, $\mu = 0$

(c) In the given sequence the increase in size (iodine atom being largest) and molecular weights are responsible for greater van der Waals' forces of attraction which overshadows the dipole-dipole attractions.

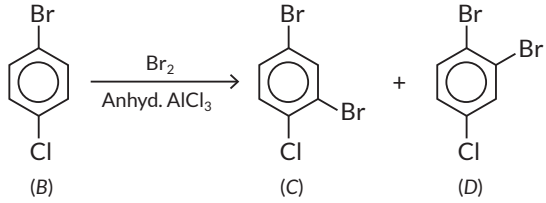
24. Since, bromine is *o*- and *p*- directing, on chlorination of bromobenzene the products are (*A* and *B*) as following:



Further, monobromination of (*A*) gives several products, thus (*A*) is *ortho* isomer :



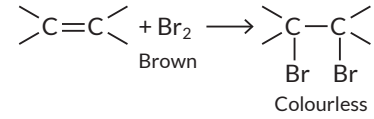
Structure of *B* : It will be the *p*-isomer as on monobromination it yields only two products :

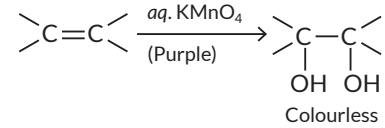


Isomer (*C*) is identical to (IV) but (*D*) does not resemble any of the structures of *A* (I to IV).

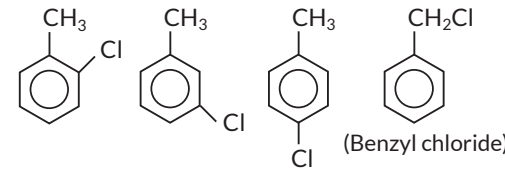
25. (i) Allyl chloride shows high reactivity as the carbocation formed by hydrolysis is stabilised by resonance while no such stabilisation of carbocation exists in the case of *n*-propyl chloride.

(ii) Presence of a double bond in a molecule can be detected by bromine water test and Baeyer's test. The molecules with a double bond decolourise bromine water and aqueous $KMnO_4$.





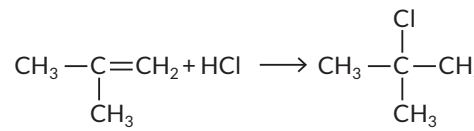
(iii)



Among these isomers, benzyl chloride has the weakest C — Cl bond. Because in all other isomers C — Cl bond has some double bond character due to resonance.

OR

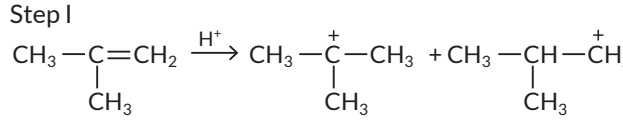
(i)



Iso-butylene 2-Chloro-2-methylpropane

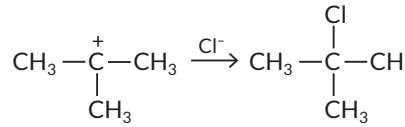
Mechanism :

Step I



3° Carbocation (more stable) 1° Carbocation (less stable)

Step II



(ii) $^{-}C \equiv N$ acts as a stronger nucleophile from carbon end because it will lead to the formation of C — C bond which is more stable than C — N bond if linkage is from N side.

(iii) Free radical halogenation of alkanes is not a suitable method to obtain an alkyl halide because :

(a) It gives a mixture of isomeric monohalogenated products whose boiling points are so close that their separation is difficult.

(b) Polyhalogenation may also occur making the product mixture more complex and hence, difficult to separate.

CHAPTER

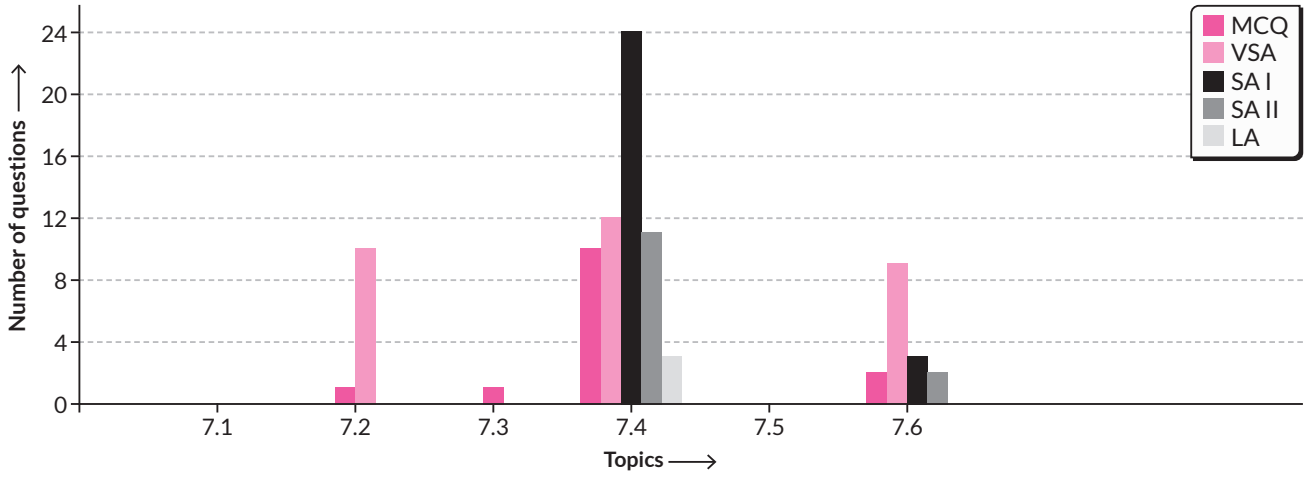
7

Alcohols, Phenols and Ethers

TOPICS

7.1 Classification
7.2 Nomenclature
7.3 Structures of Functional Groups
7.4 Alcohols and Phenols
7.5 Some Commercially Important Alcohols
7.6 Ethers

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



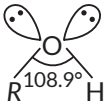
Weightage Xtract

- Topic 7.4 is highly scoring topic.
- Maximum total weightage is of topic 7.4 *Alcohols and Phenols.*
- Maximum MCQ, VSA, SA I, SA II and LA type questions were asked from topic 7.4 *Alcohols and Phenols.*

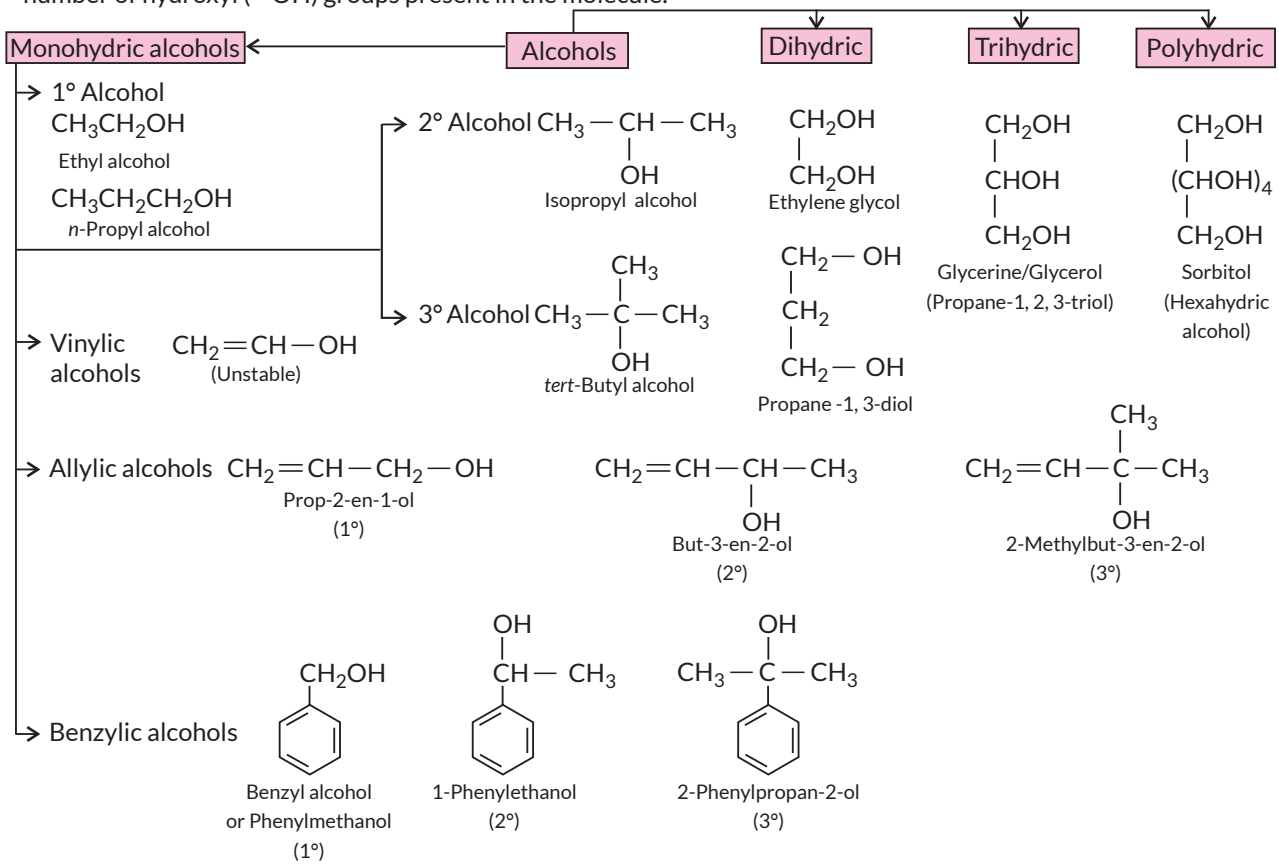
QUICK RECAP

ALCOHOLS

- **General formula :** Alcohols are the hydroxy derivatives of alkanes having general formula $C_nH_{2n+1}OH$.
- **Nomenclature :** In common system, alcohols are named as *alkyl alcohol*. According to IUPAC system, alcohols are called '*alkanols*', by replacing '*-e*' of alkane by '*-ol*'.
- **Structure :** In alcohols, *R*—OH, the O-atom of hydroxyl group is attached to C-atom by a sigma (σ) bond formed by the overlap of sp^3-hybridised orbital of C-atom with sp^3-hybridised orbital of O-atom.



Classification : Alcohols are classified as monohydric, dihydric, trihydric and polyhydric alcohols depending upon the number of hydroxyl (—OH) groups present in the molecule.



Preparation :

- **From alkenes :**
  - **By acid catalysed hydration :**

$$CH_3CH=CH_2 + H_2O \xrightleftharpoons{H^+} CH_3-CH(OH)-CH_3$$

  - **By hydroboration-oxidation :**

$$CH_3CH=CH_2 + (H\text{-}BH_2)_2 \longrightarrow CH_3-CH(H)-CH_2(BH_2)$$

$$(CH_3CH_2CH_2)_2BH \xleftarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 3CH_3CH_2CH_2OH + B(OH)_3$$

Propan-1-ol

- **From carbonyl compounds :**
  - **By reduction of aldehydes and ketones :**

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCOR' \xrightarrow{NaBH_4} R-CH(OH)-R'$$

  - **By reduction of carboxylic acids and esters :**

$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$

$$RCOOR' \xrightarrow{H^+/H_2O} RCOOH + R'OH$$

  - **From Grignard reagents :**

$$RCHO + R'MgX \xrightarrow{H_2O} R-CH(R')-OMgX \xrightarrow{H_2O} Mg(OH)X + R-CH(R')-OH$$

$$RCOR + R'MgX \longrightarrow R-C(R')(R)-OMgX \xrightarrow{H_2O} R-C(R')(R)-OH + Mg(OH)X$$

Physical properties :

- **Physical state :** Lower alcohols are colourless liquids with characteristic smell while higher alcohols are colourless, odourless waxy solids.
- **Solubility :** Solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl groups and solubility increases with increase in branching and the order is $1° < 2° < 3°$.

- **Boiling points :** The boiling points of alcohols increase with increase in the number of carbon atoms as van der Waals' forces increase and the boiling points decrease with increase of branching in carbon chain due to decrease in van der Waals' forces with decrease in surface area and the order is 1° > 2° > 3°.

Chemical properties : Alcohols react both as nucleophiles (when the bond between O — H is broken) and electrophiles (when the bond between C — O is broken).

- **Reactions involving cleavage of O—H bond :**
  - **Acidity of alcohols (reaction with metals) :**

$$2ROH + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2RONa} + H_2$$

  - The above reaction shows that alcohols are acidic in nature.
  - The acid strength of alcohols decreases in the following order :

$$R\!\rightarrow\!CH_2OH > \underset{R}{\overset{R}{\diagup\!\diagdown}}CHOH >> R\!\rightarrow\!\underset{R}{\overset{R}{\diagup\!\diagdown}}C\!-\!OH$$

Primary Secondary Tertiary

  - **Esterification :**

$$R'OH + (RCO)_2O \text{ or } R'COCl \longrightarrow \underset{\text{Ester}}{RCOOR'}$$

- **Reactions involving cleavage of C—O bond :**
  - **Reaction with hydrogen halides :**

$$ROH + HX \xrightarrow[\Delta]{\text{Anhyd. } ZnCl_2} RX + H_2O$$

  - **Lucas test :** Lucas reagent is a solution of conc. HCl with anhyd. $ZnCl_2$.
  - With Lucas reagent,
    Primary alcohols – No cloudiness
    Secondary alcohols – Cloudiness appears in 5 minutes
    Tertiary alcohols – Cloudiness appears immediately
  - **Reaction with phosphorus trihalides :**

$$ROH + PCl_3 \longrightarrow RCl + H_3PO_3$$

  - **Dehydration :**

$$C_2H_5OH \xrightarrow[443\text{ K}]{H_2SO_4} CH_2{=}\,CH_2 + H_2O$$

$$CH_3\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow[440\text{ K}]{85\%\ H_3PO_4} CH_3CH{=}CH_2 + H_2O$$

$$CH_3\!-\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\!-\!OH \xrightarrow[358\text{ K}]{20\%\ H_3PO_4} CH_3\!-\!\underset{CH_3}{\overset{CH_2}{\underset{|}{\overset{\|}{C}}}}\!-\!CH_3 + H_2O$$

Thus, the relative ease of dehydration of alcohols follows the order : Tertiary > Secondary > Primary

  - **Oxidation :**

$$RCH_2OH \xrightarrow{[O]} \underset{\text{Aldehyde}}{R\!-\!\overset{H}{\underset{|}{C}}\!=\!O} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R\!-\!\overset{OH}{\underset{|}{C}}\!=\!O}$$

$$RCH_2OH \xrightarrow{CrO_3 \text{ or } Cu/573\text{ K}} RCHO$$

$$CH_3CH{=}CHCH_2OH \xrightarrow{PCC} CH_3CH{=}CHCHO$$

$$R\!-\!\underset{OH}{\underset{|}{CH}}\!-\!R' \xrightarrow{CrO_3 \text{ or } Cu/573\text{ K}} R\!-\!\underset{O}{\overset{\|}{C}}\!-\!R'$$

sec-Alcohol Ketone

$$CH_3\!-\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\!-\!OH \xrightarrow[573\text{ K}]{Cu} \underset{\text{Isobutene}}{CH_3\!-\!\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\!=\!CH_2}$$

Some commercially important alcohols :

- **Methanol (wood spirit) :** It is produced by catalytic hydrogenation of CO in the presence of ZnO – Cr_2O_3 as catalyst at high temperature and pressure.

$$CO + 2H_2 \xrightarrow[200\text{-}300\text{ atm, }573\text{-}673\text{ K}]{ZnO - Cr_2O_3} CH_3OH$$

  - Methanol is a colourless liquid and is highly poisonous in nature.
  - Ingestion of small quantities can cause blindness while large quantities can cause death.
  - It is used as a solvent in paints, varnishes and for making formaldehyde.
- **Ethanol :** It is commercially manufactured by using fermentation of sugar present in molasses, sugarcane or fruits such as grapes.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

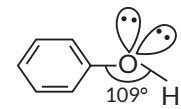
  - Ethanol is colourless liquid and is used as a solvent in paint industry and in preparation of a number of carbon compounds.
  - Commercial alcohol is made unfit for drinking by mixing it with copper sulphate and pyridine, it is called *denatured alcohol*.

PHENOLS

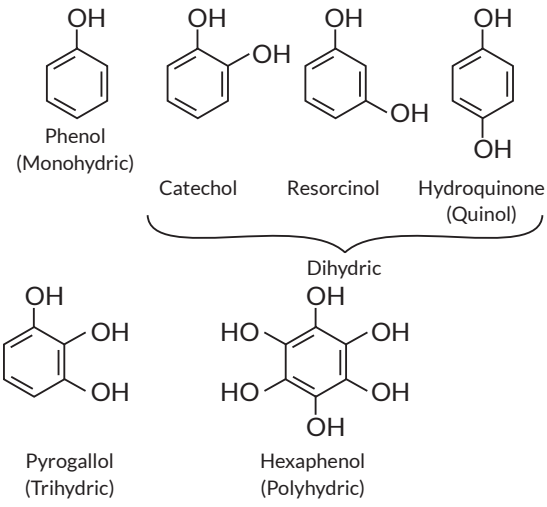
General formula : Phenols are the compounds in which hydroxy (—OH) group is directly linked to aromatic ring having formula, C_6H_5OH.

Nomenclature : The simplest hydroxy derivative of benzene is phenol, also called *carbolic acid*. It is its common name and also an accepted IUPAC name.

Structure : In phenols, the —OH group is attached to sp^2-hybridised C-atom of an aromatic ring.

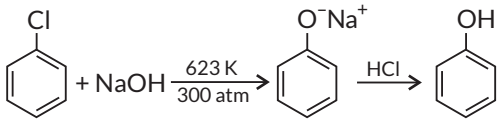


Classification : Like alcohols, phenols are also classified as monohydric, dihydric and polyhydric phenols.

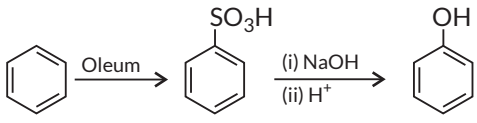


Preparation :

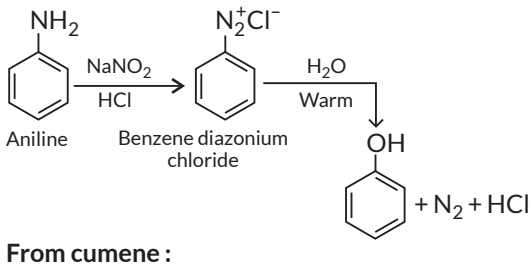
From haloarenes :



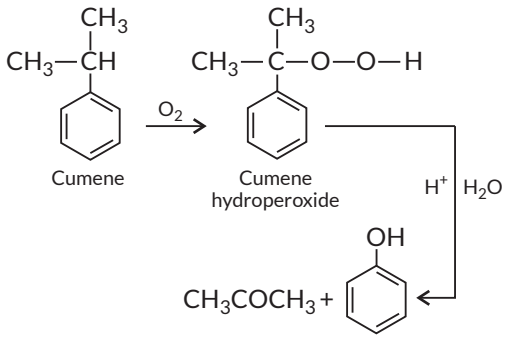
From benzene:



From diazonium salts :



From cumene :



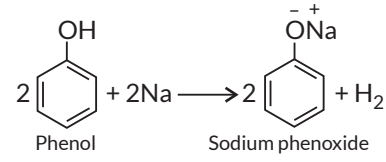
Physical properties :

- **Physical state :** Phenols are colourless crystalline solids or liquids.
- **Odour :** They have characteristic phenolic odours.
- **Solubility :** Like alcohols, phenols are soluble in water due to the formation of hydrogen bonding with water molecules.
  - Phenols are less soluble than alcohols due to large hydrocarbon (benzene ring) part.
  - Phenols are soluble in alcohols, ethers and also in NaOH.

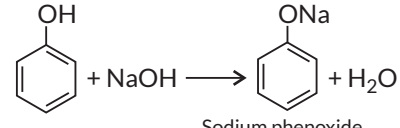
Boiling points : The boiling points of phenols are much higher than the corresponding aromatic hydrocarbons and haloarenes due to intermolecular hydrogen bonding.

Chemical properties :

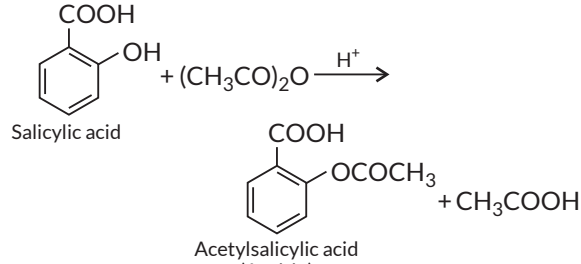
- **Acidity of phenols :** Phenols are weakly acidic in nature due to polar O—H bond directly attached to sp^2-hybridised C-atom.
  - They turn blue litmus red and react with alkali metals and alkalies to form their salts.
  - Phenol is weaker acid than carboxylic acids. It does not react with sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$).
  - Phenols are more acidic than alcohols which can be explained on the basis of resonance.
  - Electron withdrawing groups increase the acidic strength of phenols.
  - Electron releasing groups decrease the acidic strength of phenols.
  - **Reaction with metals :**



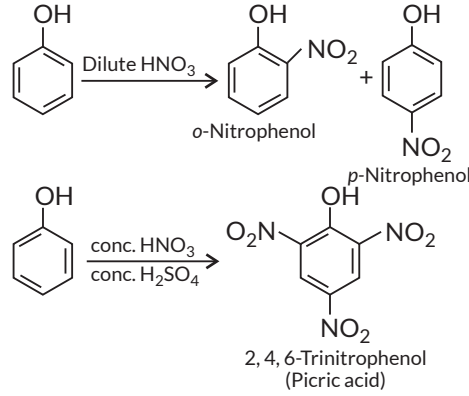
In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



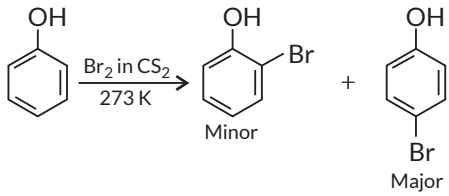
- **Esterification :**

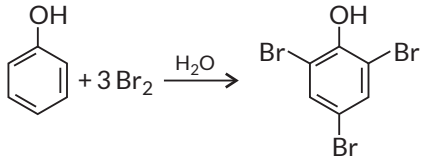


- **Electrophilic aromatic substitution :**
  - **Nitration :**



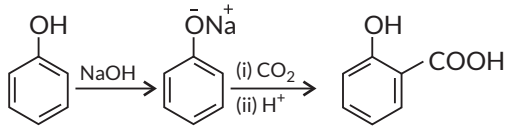
– **Halogenation :**





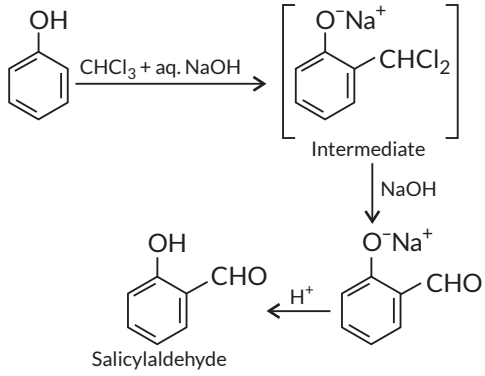
2, 4, 6-Tribromophenol

▶ **Kolbe's reaction :**



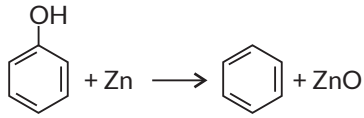
2-Hydroxybenzoic acid
(Salicylic acid)

▶ **Reimer-Tiemann reaction :**

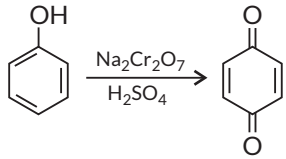


Salicylaldehyde

▶ **Reaction of phenol with zinc dust :**



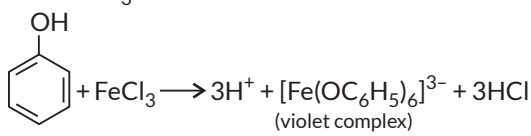
▶ **Oxidation**



Benzoquinone

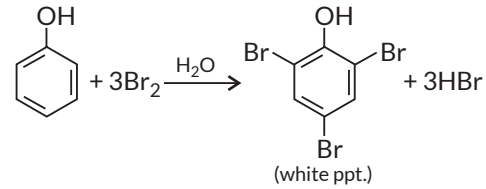
▶ **Test for phenols :**

– **Ferric chloride test :** Phenol gives violet colour with neutral $FeCl_3$ solution.



(violet complex)

– **Bromine water test :** Phenol gives white ppt. with Br_2 water due to the formation of 2,4,6-tribromophenol.



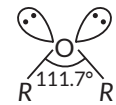
(white ppt.)

ETHERS

General formula : Ethers are the compounds having general formula, $C_nH_{2n+2}O$, where, *n* is always greater than 1.

Nomenclature : Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word '*ether*' at the end. If both the alkyl groups are the same, the prefix '*di*' is added before the alkyl group. According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an —O*R* or —OAr group, where *R* and Ar represent alkyl and aryl groups, respectively. The larger *R* group is chosen as the parent hydrocarbon.

Structure : In ethers, the four electron pairs, *i.e.*, the two bond pairs and two lone pairs of electrons on O-atom are arranged approximately in a tetrahedral arrangement.



Classification : Ethers can be classified as symmetrical or simple ethers having formula, $R-O-R$ and unsymmetrical or mixed ethers having formula, $R-O-R'$.

Preparation :

▶ **From alcohols by dehydration :**

$$2ROH \xrightarrow{H_2SO_4,\ 413\ K} ROR$$

▶ **From alkyl halides :**

$$R-X + R'ONa \xrightarrow[-NaX]{\Delta} ROR' \quad \text{(Williamson synthesis)}$$

– Williamson synthesis can be used to prepare ethers containing 2° or 3° alkyl groups through S_N2 mechanism. In this case, the alkyl halide must be 1°. In the case of 2° and 3° alkyl halides, elimination takes place. It cannot be used to prepare diaryl ethers.

– Dehydration of alcohols for the formation of ethers follows the order : 1° > 2° > 3°

Physical properties :

▶ **Physical state and odour :** Dimethyl ether and ethyl methyl ether are exceptionally gases at room temperature while all other ethers are colourless liquids with characteristic ethereal smell.

▶ **Solubility :** Ethers are soluble in water to a certain extent due to hydrogen bonding.

– Solubility decreases with increase in molecular mass.

– Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene, etc.

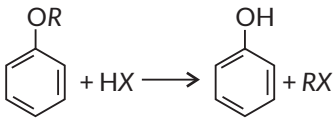
- **Boiling points :** Ethers have lower boiling points than isomeric alcohols due to their inability to form hydrogen bonds and get associated.
  - But lower ethers have slightly higher boiling points than *n*-alkanes of comparable molecular masses due to dipole-dipole interactions.
  - Higher ethers (containing carbon atom more than four) have slightly lower boiling points than *n*-alkanes of comparable molecular masses due to weak van der Waals' forces of attraction.
- **Polarity :** Ethers are polar in nature.
- **Density :** Ethers have low density. All ethers are lighter than water.

Chemical properties :

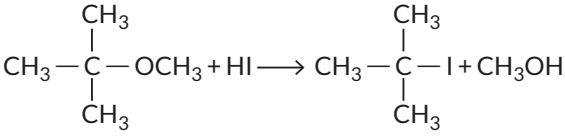
- **Cleavage of C—O bond in ethers :**

$ROR' + HX \longrightarrow RX + R'OH$

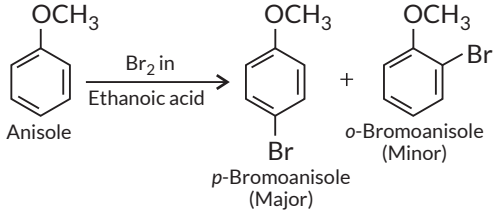
$R'OH + HX \longrightarrow R' - X + H_2O$



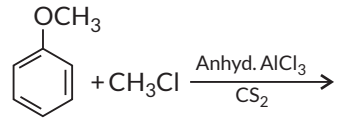
The order of reactivity of hydrogen halides is as follows : HI > HBr > HCl.

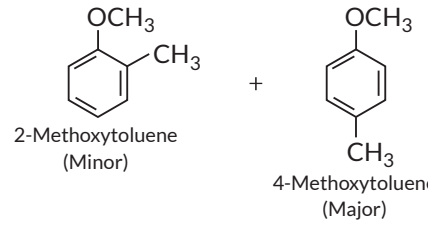


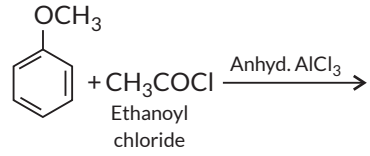
- **Electrophilic substitution :**
  - **Halogenation :**

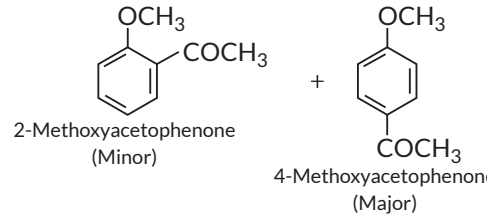


  - **Friedel-Crafts reaction :**

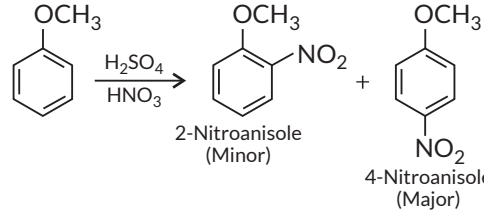








  - **Nitration :**



ALCOHOL, PHENOLS AND ETHERS

Alcohols and Phenols

IUPAC name : Alcohol → alkanol

$C_nH_{2n+1}OH$ (for monohydric alcohol)

Structure

142 pm, 96 pm, 108.9°, sp^3

Classification

C_{sp^3} —OH bond

- **1°** : —OH attached to 1° C, $—CH_2OH$
- **2°** : —OH attached to 2° C, $>CH—OH$
- **3°** : —OH attached to 3° C, $>C—OH$
- **Allylic :** $>C=CH—CH_2—OH$
- **Benzylic :** $C_6H_5—CH_2—OH$

C_{sp^2} —OH bond

- **Vinylic :** $>C=CH—OH$
- **Arylic :** $C_6H_5—OH$(Phenol)

Distinction test for phenol

Test	Observation
$FeCl_3$ test	Violet colour
Br_2-H_2O test	White ppt.
Liebermann's nitroso test ($NaNO_2$ + conc. H_2SO_4)	Deep green/blue colour which changes into red on dilution
Ammonia/Sodium hypochlorite test	Blue colour
Azo dye test	Orange colour

Ethers

IUPAC name : alkoxyalkanes

Structure

141 pm, 110°, sp^3

Classification

Simple or Symmetrical
Two alkyls attached to oxygen are same

Mixed or Unsymmetrical
Different alkyls are attached to oxygen

Properties

Physical

- B.P. ∝ no. of C atoms
- B.P. ∝ 1/branching
- B.P. of alcohols and phenols are higher than that of hydrocarbons, ethers, haloalkanes, haloarenes.
- Solubility ∝ 1/size of alkyl or aryl groups.
- Soluble in water due to H-bonding

Chemical

Cleavage of O–H bond :

- $2R-OH + 2Na \rightarrow 2R-O-Na + H_2$
  Act as nucleophiles.
- **Ease of cleavage of O–H bond :** phenols > 1° alcohols > 2° > 3°.
- **Acidity :** phenols > H_2O > alcohols.
- EWG increases acidity, EDG decreases acidity.

Cleavage of C – OH bond :

- **Order of reactivity :** 3° > 2° > 1°.

$R-OH \xrightarrow[\text{anhy. } ZnCl_2,\ \Delta]{HX} R-X$; $\xrightarrow[P X_3]{} R-X$; $\xrightarrow{SOCl_2,\ \text{Pyridine}} R-Cl$; $\xrightarrow[633K]{NH_3,\ Al_2O_3} R-NH_2$

Reactions involving whole alcohol molecule :

- **Dehydration :** $R-OH$ + conc. H_2SO_4 → 433K → Alkene; 413 K → Ether; 383 K → Alkyl hydrogen sulphate
- **Oxidation :** 1° alcohol $\xrightarrow{[O]}$ Aldehyde $\xrightarrow{[O]}$ Carboxylic acid (Cu/573 K)

Electrophilic substitution of phenols :
Halogenation, sulphonation, nitration, Friedel-Crafts alkylation, etc. occurs at *o*- and *p*-positions due to activating effect of –OH group.

Properties

Physical

- C – O bonds → slightly polar.
- B.P. lower than isomeric alcohols.
- Sparingly soluble in water.
- Solubility ∝ 1/molecular mass.
- Lighter than water.

Chemical

Reaction of etheral oxygen :

$ROR + HCl \xrightarrow[\text{conc.}]{} \left[R-\overset{+}{O}(H)-R\right] Cl^-$

Cleavage of C – O bond :

$R-OR + HX \xrightarrow{373\ K} R-OH + R-X$

In case of alkyl aryl ethers, phenol and an alkyl halide are obtained.

- $ROR + H_2O \xrightarrow[\Delta]{\text{dil. } H_2SO_4} 2R-OH$
- $ROR + PX_5 \xrightarrow{\Delta} 2R-X$

Reaction involving alkyl group :

- Formation of peroxides with air and light.
- Substitution products obtained on halogenation.

Electrophilic substitution reaction :
In aryl ethers, +*R* effect of alkoxy group (–*OR*) activates the benzene ring → substitution occurs at *o*- and *p*-positions.

Distinction test for alcohol

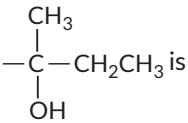
Alcohol	Dichromate (Oxidation) test	Victor Meyer test	Lucas test
1°	Acid (Orange solution becomes green)	Blood red colour	No turbidity
2°	Ketone (Orange solution becomes green)	Blue colour	Turbidity in 5 minutes
3°	No reaction	Colourless	Turbidity immediately

BRAIN MAP

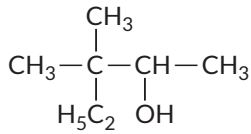
Previous Years' CBSE Board Questions

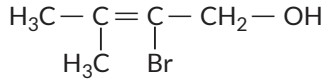
7.2 Nomenclature

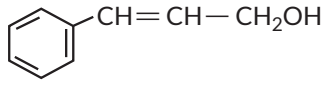
MCQ

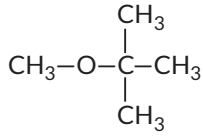
1. The correct IUPAC name of  is
   (a) *tert*-butyl alcohol
   (b) 2,2-Dimethylpropanol
   (c) 2-Methylbutan-2-ol
   (d) 3-Methylbutan-3-ol *(2020)*

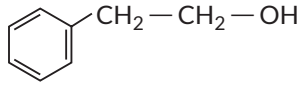
VSA (1 mark)

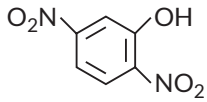
2. Write the IUPAC name of the following :

(2018) Ap

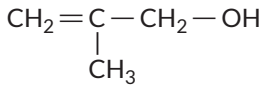
3. Write the IUPAC name of the following compound :

(AI 2017)

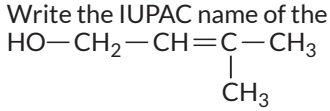
4. Write the IUPAC name of the following compound :

(AI 2017) Ap

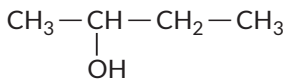
5. Write the IUPAC name of the following compound :

(AI 2017)

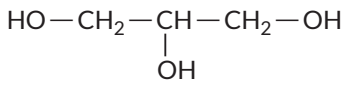
6. Write the IUPAC name of the given compound.

(AI 2016)

7. Write the IUPAC name of the given compound :

(Delhi 2015) Ap

8. Write the IUPAC name of the given compound :

(AI 2015)

9. Write the IUPAC name of the given compound:

(Foreign 2015)

10. Name the following according to IUPAC system :

(1/2, Delhi 2015C)

11. Write IUPAC name of the following compound :

(Foreign 2014)

7.3 Structures of Functional Groups

MCQ

12. The C — O — H bond angle in alcohol is
   (a) slightly greater than 109°28′
   (b) slightly less than 109°28′
   (c) slightly greater than 120°
   (d) slightly less than 120° *(Term I, 2021-22)* U

13. **Assertion (A) :** The C — O — H bond angle in alcohols is slightly less than the tetrahedral angle.
   Reason (R) : This is due to the repulsive interaction between the two lone electron pairs on oxygen.
   (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
   (d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)* Ap

7.4 Alcohols and Phenols

MCQ

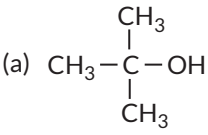
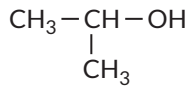
14. Which of the following alcohols will not undergo oxidation?
   (a) Butanol (b) Butan-2-ol
   (c) 2-Methylbutan-2-ol (d) 3-Methylbutan-2-ol
   (2023)

15. In the reaction $R - OH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$, what is the correct order of reactivity of alcohol?
   (a) 1° < 2° < 3° (b) 1° > 3° > 2°
   (c) 1° > 2° > 3° (d) 3° > 1° > 2°
   (2023)

Read the passage given below and answer the following questions (Q. No. 16 to 18) :

Alcohols and phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron donating groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to give alkyl halides. On oxidation primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. The presence of — OH groups in phenols activates the ring towards electrophilic substitution. Various important products are obtained from phenol like salicylaldehyde, salicylic acid, picric acid etc.

16. Which of the following alcohols is resistant to oxidation?

(a)  (b) 

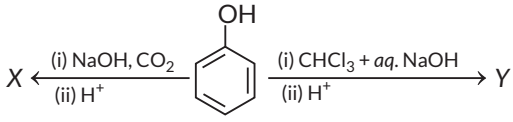
(c) CH_3-CH_2-OH (d) CH_3-OH An

17. Which of the following groups increases the acidic character of phenol?

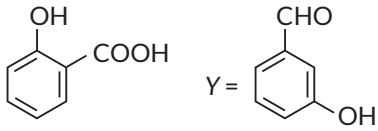
(a) CH_3O^- (b) CH_3^-

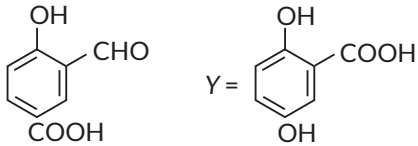
(c) NO_2^- (d) All of these An

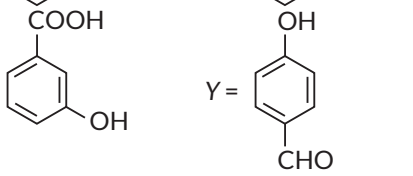
18. Consider the following reaction:

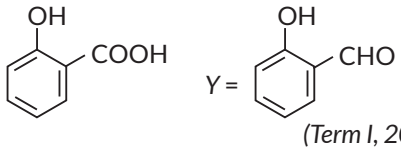


the products *X* and *Y* are

(a) 

(b) 

(c) 

(d) 

(Term I, 2021-22)

19. In the following reaction,

$CH_3-CH=CH-CH_2-OH \xrightarrow{PCC}$

the product formed is

(a) CH_3-CHO and CH_3CH_2OH

(b) $CH_3-CH=CH-COOH$

(c) $CH_3-CH=CH-CHO$

(d) $CH_3-CH_2-CH_2-CHO$

(Term I, 2021-22) U

20. Which of the following acids reacts with acetic anhydride to form aspirin?

(a) Benzoic acid (b) Salicylic acid

(c) Phthalic acid (d) Acetic acid

(Term I, 2021-22)

21. **Assertion (A) :** *o*-nitrophenol is a weaker acid than *p*-nitrophenol.

Reason (R) : Intramolecular hydrogen bonding makes *ortho* isomer weaker than *para* isomer.

(a) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the assertion (A).

(b) Both assertion (A) and reason (R) are correct statements, but reason (R) is not the correct explanation of the assertion (A).

(c) Assertion (A) is correct, but reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but reason (R) is correct statement. *(2020)*

22. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as

(a) a dehydrohalogenation reaction

(b) a substitution reaction

(c) an addition reaction

(d) a dehydration reaction *(2020)*

23. **Assertion (A) :** Alcohols have higher boiling point than alkanes of comparable molecular mass.

Reason (R) : Alcohols have intramolecular hydrogen bond.

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020C)*

VSA (1 mark)

24. Carry out the following conversion :

Phenol to salicylaldehyde *(1/5, 2020)*

25. Carry out the following conversion :

Propene to propanol *(1/5, 2020)* Cr

26. Predict the reagent for carrying out the following conversion :

Phenol to benzoquinone *(1/5, 2020, 2019)*

27. Predict the reagent for carrying out the following conversion :

Phenol to 2,4,6-tribromophenol *(1/5, 2020)*

28. Write the preparation of phenol from cumene. *(1/3, 2020)*

29. How can you convert the following?

Phenol to chlorobenzene. *(1/3, 2020)* Cr

30. How can you convert the following?

Sodium phenoxide to *o*-hydroxybenzoic acid. *(1/3, 2020)*

OR

Write the equation involved in the following reaction:

Kolbe's reaction *(1/2, AI 2019, Delhi 2014C)*

31. How can you convert the following?

Ethanol to propanenitrile. *(1/3, 2020)*

32. Give reason for the following :
Phenol is more acidic than ethanol.
(1/3, AI 2017C, 2015) An

33. Write the equation involved in the acetylation of salicylic acid.
(Delhi 2015)

34. Which of the following isomers is more volatile :
o-nitrophenol or *p*-nitrophenol?
(Delhi 2014) An

35. Write the equation involved in the following reaction :
Reimer –Tiemann reaction. *(1/2, AI 2014)*

SA I (2 marks)

36. Predict the products of the following reactions :
(i) $CH_3CH_2OH \xrightarrow{Cu/573\ K}$
(ii) $C_6H_5OH \xrightarrow{Br_{2(aq)}}$ *(2023)*

37. For the pair phenol and cyclohexanol, answer the following:
(a) Why is phenol more acidic than cyclohexanol?
(b) Give one chemical test to distinguish between the two. *(2023)*

38. Account for the following :
(i) Phenol is a stronger acid than an alcohol.
(ii) The boiling point of alcohols decreases with increase in branching of alkyl chain.

OR

(i) Write the mechanism of the following reaction
$CH_3CH_2OH \xrightarrow[443\ K]{H^+} CH_2=CH_2 + H_2O$
(ii) Write the equation involved in Reimer-Tiemann reaction. *(2023)*

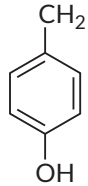
39. Write structures of the products formed when :
(i) Propan-2-ol is heated with Cu at 573 K.
(ii) Salicylic acid is treated with $(CH_3CO)_2O/H^+$.
(2021C)

40. Carry out the following conversions :
(i) Phenol to Anisole
(ii) Aniline to Phenol *(2021C)*

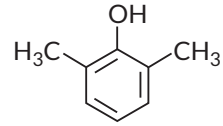
41. Out of *t*-butyl alcohol and *n*-butanol, which one will undergo acid catalysed dehydration faster and why?
(2/5, 2020) An

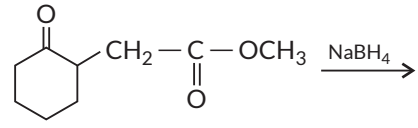
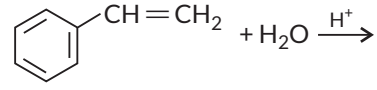
42. How are the following conversions carried out?
(i) Propene to propan-2-ol
(ii) Benzyl chloride to benzyl alcohol
(2020C, 2/3, Delhi 2015C) Ap

43. Give the mechanism for the formation of ethanol from ethene.
(2/5, 2020, AI 2015)

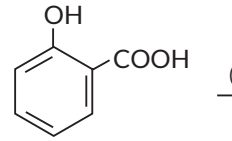
44. Write the major product(s) of the following reactions :
(i)  $\xrightarrow[\Delta]{HCl}$; (ii) $(CH_3)_3COH \xrightarrow[573\ K]{Cu}$
(2/3, 2020) U

45. How do you convert the following ?
(a) Phenol to Toluene
(b) Ethanol to Ethanal *(2019)*

46. (a) Show the chemical reaction with bond movements and arrows for the nucleophilic attack of water on carbocation in acid catalysed hydration of alkenes.
(b) Give IUPAC name for the following :

(2019C)

47. Write the structures of the main products in the following reactions :
(i) 
(ii) 
(2/3, 2018) Ap

48. Explain the mechanism of dehydration steps of ethanol.
$CH_3CH_2OH \xrightarrow[443\ K]{H^+} CH_2=CH_2+H_2O$
(2/3, 2018C, Delhi 2015C)

49. Write the product(s) in the following reactions :
(i)  $\xrightarrow[H^+]{(CH_3CO)_2O}$?
(ii) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC}$?
(2/5, Delhi 2017)

50. Give simple chemical tests to distinguish between the following pairs of compounds :
(i) Ethanol and phenol
(ii) Propanol and 2-methylpropan-2-ol.
(2/5, Delhi 2017)

51. (a) Arrange the following compounds in the increasing order of their acid strength :
p-cresol, *p*-nitrophenol, phenol
(b) Write the mechanism (using curved arrow notation) of the following reaction :
$CH_2=CH_2 \xrightarrow{H_3O^+} CH_3-CH_2^+ + H_2O$ *(AI 2017)*

52. Write the structure of the products when butan-2-ol reacts with the following :
(a) CrO_3
(b) $SOCl_2$ *(AI 2017)* Ap

53. Write the main product(s) in each of the following reactions :
(i) $CH_3-CH=CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6}$
(ii) $C_6H_5-OH \xrightarrow[(ii)\ CO_2, H^+]{(i)\ aq.\ NaOH}$ *(Delhi 2016)*

54. Write the final product(s) in each of the following reactions :

(i) $CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573\ K}$

(ii) $C_6H_5-OH \xrightarrow[(ii)\ H^+]{(i)\ CHCl_3 + aq.\ NaOH}$ *(Delhi 2016)*

55. Write the mechanism of the following reaction :

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

(AI 2014, 2/3, Foreign 2014)

56. Name the reagents used in the following reactions :

(i) Bromination of phenol to 2, 4, 6-tribromophenol

(ii) Butan-2-one to Butan-2-ol

(iii) Friedel–Crafts alkylation of anisole

(iv) Oxidation of primary alcohol to carboxylic acid

(Foreign 2014) Cr

57. Name the different reagents needed to perform the following reactions :

(i) Phenol to Benzene

(ii) Dehydration of propan-2-ol to propene

(iii) Friedel-Crafts alkylation of anisole

(iv) Dehydrogenation of ethanol to ethanal

(Foreign 2014)

58. How are the following conversions carried out?

(i) Propene to Propan-2-ol

(ii) Ethyl chloride to Ethanal *(Delhi 2014C)*

59. Explain the following with an example for each :

(i) Kolbe's reaction,

(ii) Reimer-Tiemann reaction *(2/3, AI 2014C)* R

SA II (3 marks)

60. (i) Why is the C—O bond length in phenol less than that in methanol?

(ii) Arrange the following in order of increasing boiling point:
Ethoxyethane, Butanal, Butanol, *n*-Butane

(iii) How can phenol be prepared from anisole? Give reaction. *(2023)*

61. How do you convert the following : (Any three)

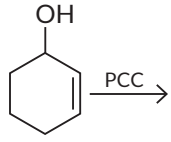
(a) Phenol to picric acid

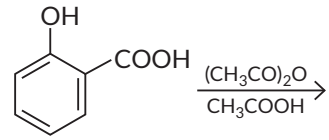
(b) Propanone to 2-methylpropan-2-ol

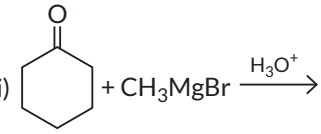
(c) Phenol to anisole

(d) Propene to propan-1-ol *(2023)*

62. Write the product(s) of the following reactions :

(i) 

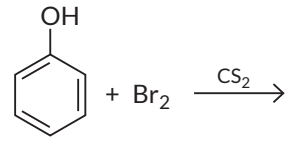
(ii) 

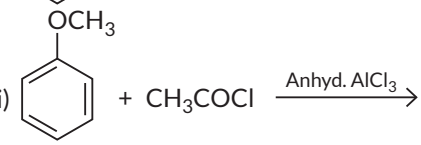
(iii) 

(2020) Ap

63. Write the products of the following reactions :

(i) $CH_3-CH_2-O-CH_3 + HI \longrightarrow$

(ii) 

(iii) 

(2019)

64. Give one chemical test to distinguish between the following :

(a) Phenol and 1-propanol

(b) Ethanol and dimethyl ether

(c) 1-propanol and 2-methyl-2-propanol *(2019)*

65. (a) Show how will you synthesise the following alcohol prepared by the reaction of a suitable Grignard reagent on methanal?

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$

(b) Write the mechanism of the following reaction :

$CH_2=CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$ *(AI 2019)*

66. (a) How will you convert the following :

(i) Phenol to benzoquinone

(ii) Propanone to 2-methylpropan-2-ol

(b) Why does propanol have higher boiling point than that of butane ? *(2019C)*

67. How do you convert the following?

(i) Phenol to anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol *(Delhi 2015)*

68. Predict the products of the following reactions :

(i) $CH_3-CH=CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} ?$

(ii) $C_6H_5OH \xrightarrow{Br_2(aq)} ?$

(iii) $CH_3CH_2OH \xrightarrow{Cu/573K} ?$ *(Foreign 2015)*

69. How are the following conversions carried out?

(i) Benzyl chloride to benzyl alcohol

(ii) Ethyl magnesium chloride to propan-1-ol

(iii) Propene to propan-2-ol. *(AI 2015C, 2014C)*

70. (a) Write the mechanism of the following reaction :

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

(b) Write the equation involved in Reimer–Tiemann reaction. *(Delhi 2014)*

LA (5 marks)

71. (a) How do you convert the following :
(i) Phenol to anisole
(ii) Ethanol to propan-2-ol?
(b) Write mechanism of the following reaction :

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2=CH_2 + H_2O$$

(c) Why phenol undergoes electrophilic substitution more easily than benzene?
(Delhi 2019)

72. (a) Account for the following :
(i) *o*-nitrophenol is more steam volatile than *p*-nitrophenol.
(ii) *t*-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of *t*-butylmethylether.
(b) Write the reaction involved in the following :
(i) Reimer—Tiemann reaction
(ii) Friedal—Crafts alkylation of phenol
(c) Give simple chemical test to distinguish between ethanol and phenol. *(Delhi 2019)* An

73. (a) Write the formula of reagents used in the following reactions :
(i) Bromination of phenol to 2,4,6- tribromophenol
(ii) Hydroboration of propene and then oxidation to propanol.
(b) Arrange the following compound groups in the increasing order of their property indicated :
(i) *p*-nitrophenol, ethanol, phenol (acidic character)
(ii) propanol, propane, propanal (boiling point)
(c) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} ?$$

$$CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 + H_2O$$

(Delhi 2017) Ap

7.6 Ethers

MCQ

74. **Assertion (A) :** $(CH_3)_3C-O-CH_3$ gives $(CH_3)_3C-I$ and CH_3OH on treatment with HI.
Reason (R) : The reaction occurs by S_N1 mechanism.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

75. **Assertion (A) :** The C-O-C bond angle in ethers is slightly less than tetrahedral angle.
Reason (R) : Due to the repulsive interaction between the two alkyl groups in ethers.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is wrong statement.
(d) Assertion (A) is wrong, but Reason (R) is correct statement. *(2020)* Ap

VSA (1 mark)

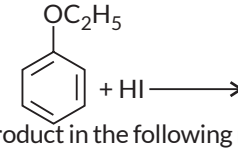
76. Carry out the following conversion :
t-Butyl chloride to *t*-butyl ethyl ether*(1/3, 2020)* Cr

77. Predict the reagent for carrying out the following conversions :
Anisole to *p*-bromoanisole *(1/3, 2020)*

78. Write the equation for the preparation of 2-methyl-2-methoxypropane by Williamson synthesis.
(1/3, 2020)

79. Write the equations involved in the following reaction :
Friedel—Crafts alkylation of anisole. *(1/2, AI 2019)*

80. Write the structure of the main products in the following reaction :



(1/3, 2018)

81. Write the product in the following reaction :

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-O-CH_2-CH_3 \xrightarrow{HI} ? + ?$$

(1/5, Delhi 2017)

82. Write the main product(s) in the following reaction :

$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3 + HI \longrightarrow$$

(1/3, Delhi 2016, 1/2, AI 2016)

83. How is the following conversion carried out?
Anisole to *p*-bromoanisole *(1/3, Delhi 2015C)*

84. Write the equation involved in the following reaction :
Williamson synthesis
(1/2, AI 2014, Delhi 2014C, 1/3, AI 2014C)

SA I (2 marks)

85. Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow[413\ K]{H^+} CH_3CH_2OCH_2CH_3 + H_2O$$

(2/3, 2020, 2/3, AI 2017, Delhi 2016, 2015)

86. Predict the major product obtained when *t*-butyl

bromide reacts with sodium methoxide. Also, give its IUPAC name. *(2019C)*

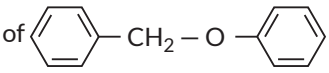
87. Give reasons for the following :
(i) Boiling point of ethanol is higher in comparison to methoxymethane.
(ii) $(CH_3)_3C-O-CH_3$ on reaction with HI gives CH_3OH and $(CH_3)_3C-I$ as the main products and not $(CH_3)_3C-OH$ and CH_3I. *(2/3, AI 2015)* An

SA II (3 marks)

88. (i) Give mechanism of the following reaction

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} CH_3CH_2-O-CH_2CH_3 + H_2O$$

(ii) Illustrate hydroboration – oxidation reaction with an example. *(2023)*

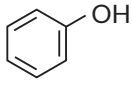
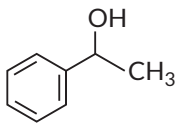
89. Give the structures of final products expected from the following reactions :
(i) Hydroboration of propene followed by oxidation with H_2O_2 in alkaline medium.
(ii) Dehydration of $(CH_3)_3C-OH$ by heating it with 20% H_3PO_4 at 358 K.
(iii) Heating of  with HI.

(2020) An

CBSE Sample Questions

7.2 Nomenclature

MCQ

1. Identify the secondary alcohols from the following set:
(i) $CH_3CH_2CH(OH)CH_3$
(ii) $(C_2H_5)_3COH$
(iii) 
(iv) 

(a) (i) and (iv) (b) (i) and (iii)
(c) (i) and (ii) (d) (i), (iii) and (iv)
(Term I, 2021-22)

7.4 Alcohols and Phenols

MCQ

2. The major product of acid catalysed dehydration of 1-methylcyclohexanol is
(a) 1-methylcyclohexane
(b) 1-methylcyclohexene
(c) 1-cyclohexylmethanol
(d) 1-methylenecyclohexane. *(2022-23)*

3. The boiling points of alcohols are higher than those of hydrocarbons of comparable masses due to
(a) hydrogen bonding
(b) ion-dipole interaction
(c) dipole-dipole interaction
(d) van der Waals' forces. *(Term I, 2021-22)*

4. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is
(a) protonation of alcohol molecule
(b) formation of carbocation
(c) elimination of water
(d) formation of an ester. *(Term I, 2021-22)*

5. Which of the following reactions is used to prepare salicylaldehyde?
(a) Kolbe's reaction
(b) Etard reaction
(c) Reimer- Tiemann reaction
(d) Stephen's reduction *(Term I, 2021-22)*

6. Lower molecular mass alcohols are
(a) miscible in limited amount of water
(b) miscible in excess of water
(c) miscible in water in all proportions
(d) immiscible in water. *(Term I, 2021-22)*

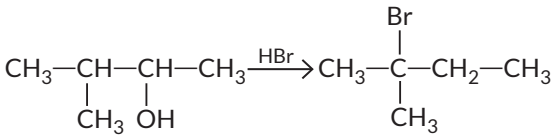
7. Phenol does not undergo nucleophilic substitution reaction easily due to
(a) acidic nature of phenol
(b) partial double bond character of C—OH bond
(c) partial double bond character of C—C bond
(d) instability of phenoxide ion. *(Term I, 2021-22)*

8. What would be the reactant and reagent used to obtain 2,4-dimethylpentan-3-ol?
(a) Propanal and propyl magnesium bromide
(b) 3-Methylbutanal and 2-methyl magnesium iodide
(c) 2-Dimethylpropanone and methyl magnesium iodide
(d) 2-Methylpropanal and *iso*-propyl magnesium iodide *(Term I, 2021-22)*

9. *o*-Hydroxybenzyl alcohol when reacted with PCl_3 gives the product as (IUPAC name)
(a) *o*-hydroxybenzyl chloride
(b) 2-(chloromethyl) phenol
(c) *o*-chloromethylchlorobenzene
(d) 4-hydroxymethyl phenol. *(Term I, 2021-22)*

SA I (2 marks)

10. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place :



Give a mechanism for this reaction. *(2020-21)*

7.6 Ethers

MCQ

11. What would be the major product of the following reaction?

$C_6H_5 - CH_2 - OC_6H_5 + HBr \rightarrow A + B$

(a) $A = C_6H_5CH_2OH$, $B = C_6H_6$

(b) $A = C_6H_5CH_2OH$, $B = C_6H_5Br$

(c) $A = C_6H_5CH_3$, $B = C_6H_5Br$

(d) $A = C_6H_5CH_2Br$, $B = C_6H_5OH$ *(2022-23)*

12. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A) : An ether is more volatile than an alcohol of comparable molecular mass.

Reason (R) : Ethers are polar in nature.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true. *(2022-23)*

13. Williamson's synthesis of preparing dimethyl ether is a/an

(a) S_N1 reaction

(b) elimination reaction

(c) S_N2 reaction

(d) nucleophilic addition reaction.

(Term I, 2021-22)

14. **Assertion :** Methoxyethane reacts with HI to give ethanol and iodomethane.

Reason : Reaction of ether with HI follows S_N2 mechanism.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement. *(2020-21)*

SA II (3 marks)

15. Write the equations for the following reactions:

(a) Salicylic acid is treated with acetic anhydride in the presence of conc. H_2SO_4.

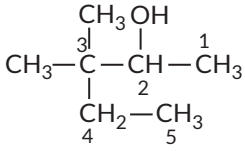
(b) *tert*-Butyl chloride is treated with sodium ethoxide.

(c) Phenol is treated with chloroform in the presence of NaOH. *(2022-23)*

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

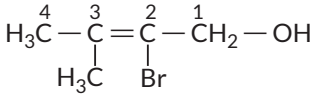
1. (c) : 2-Methylbutan-2-ol

2. 

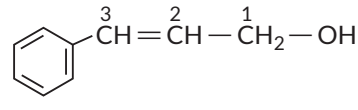
3,3 – Dimethylpentan-2-ol

Commonly Made Mistake

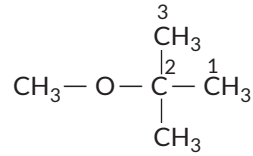
➲ Always identify longest carbon chain.

3. 

2-Bromo-3-methylbut-2-en-1-ol

4. 

3-Phenylprop-2-en-1-ol

5. 

2-Methoxy-2-methylpropane

6. 2-Phenylethan-1-ol

7. 2,5-Dinitrophenol

Answer Tips

➲ Take phenol as a parent compound.

8. 2-Methylprop-2-en-1-ol

9. 3-Methylbut-2-en-1-ol

10. Butan-2-ol

11. Propane-1,2,3-triol

12. (b): C — O — H bond angle in alcohol is 108°9′ which is slightly less than 109°28′.

13. (a): The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle due to greater lone pair-lone pair repulsions than lone pair-bond pair repulsions.

Answer Tips

➲ Apply VSEPR theory.

14. (c): Butanol : $CH_3-CH_2-CH_2-CH_2-OH$ (1° alcohol)

Butan-2-ol : $CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ (2° alcohol)

2-Methylbutan-2-ol : $H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-CH_2-CH_3$ (3° alcohol)

3-Methylbutan-2-ol : $CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ (2° alcohol)

3° alcohol does not undergo oxidation, hence in 2-methylbutan-2-ol, oxidation is not possible.

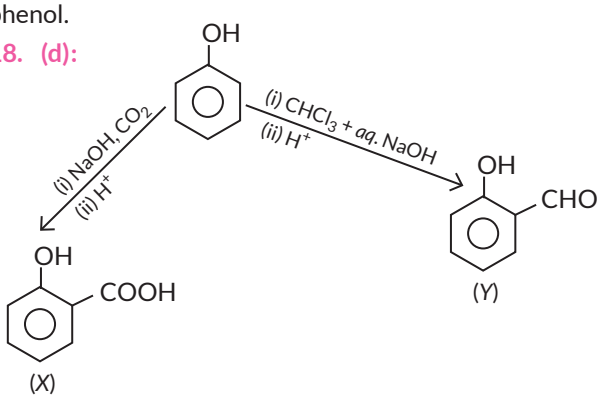
15. (a): $ROH + HX \xrightarrow[\Delta]{\text{Anhyd. } ZnCl_2} RX + H_2O$

This is a nucleophilic substitution reaction in which –OH group gets replaced by –*X* group. It involves formation of carbocation. As we know, with Lucas reagent,
Primary alcohols – No cloudiness
Secondary alcohols – Cloudiness appears in 5 minutes
Tertiary alcohols – Cloudiness appears immediately
Thus, the reactivity order is 3° > 2° > 1°.

16. (a): Tertiary alcohols do not undergo oxidation.

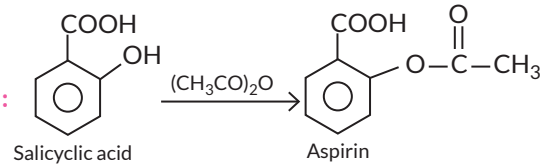
17. (c): —NO_2 acts as EWG and increases the polarity of O — H bond resulting in increased acidic character of phenol.

18. (d):



19. (c): $CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$

20. (b):



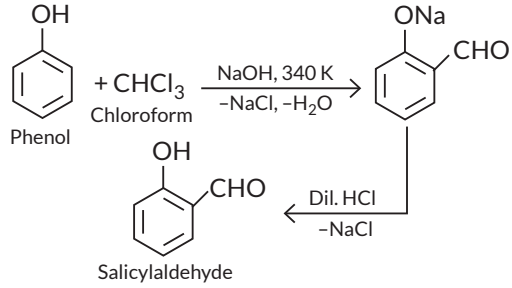
21. (a): Intramolecular H-bonding present in *o*-nitrophenol makes it weaker acid than *p*-nitrophenol.

22 (b): $RX + NaOH \rightarrow ROH + NaX$

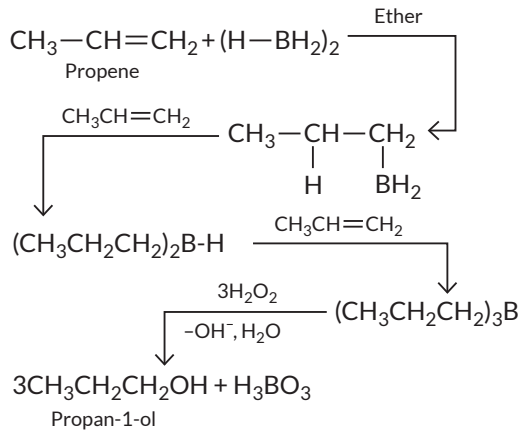
This is a substitution reaction.

23. (a): In alcohols, intramolecular hydrogen bonding is present, resulting in higher boiling point than alkanes of comparable molecular mass.

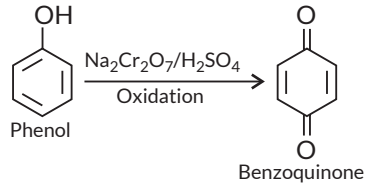
24.



25.



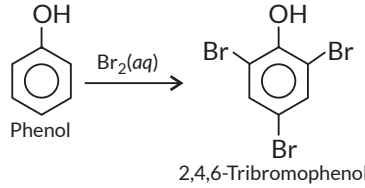
26.

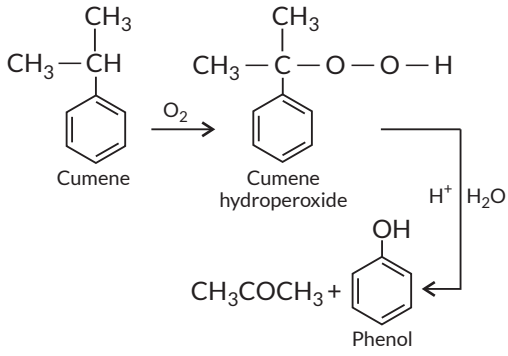


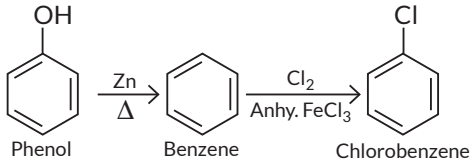
Answer Tips

➲ $Na_2Cr_2O_7/H_2SO_4$ is an oxidising agent.

27.



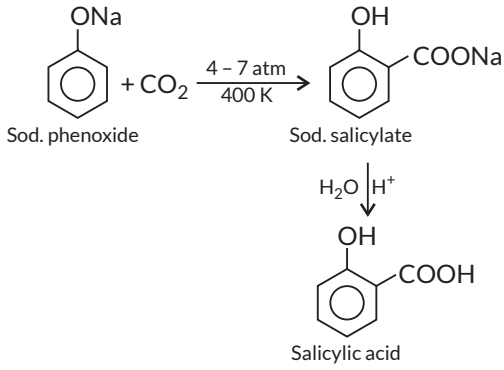
28. 

29. 

Key Points

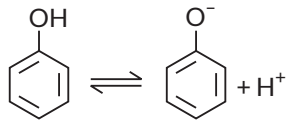
- Benzene undergoes electrophilic substitution reaction with Cl_2/anhy. $FeCl_3$.

30. **Kolbe's reaction :** When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



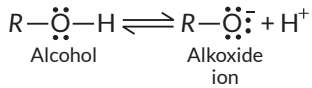
31. $CH_3CH_2OH \xrightarrow[Br_2]{Red\ P} CH_3CH_2Br \xrightarrow{NaCN} CH_3CH_2CN$
Ethanol — Ethyl bromide — Propanenitrile

32. Phenol is more acidic than alcohol. It can be explained on the basis of that alcohol on losing H^+ ions forms alkoxide ion and phenol forms phenoxide ion.
The greater acidity of phenol is due to the stability of the phenoxide ion which is resonance stabilised.



Resonance stabilised

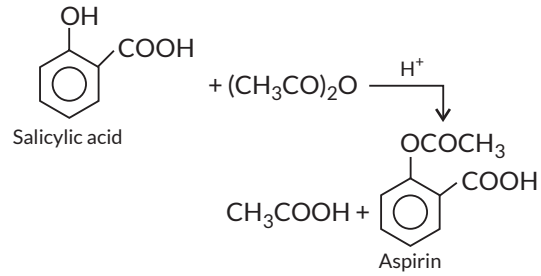
On the other hand, alkoxide ion shows no such resonance stabilisation.



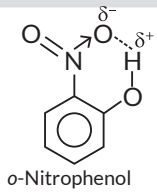
Alcohol — Alkoxide ion

Commonly Made Mistake

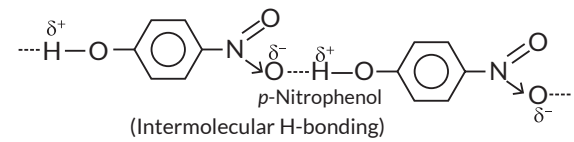
- More stable the conjugate base, higher is the acidity.

33. 

34. *o*-Nitrophenol is more volatile than *p*-nitrophenol due to the presence of intramolecular H-bonding. *p*-Nitrophenol shows intermolecular H–bonding.



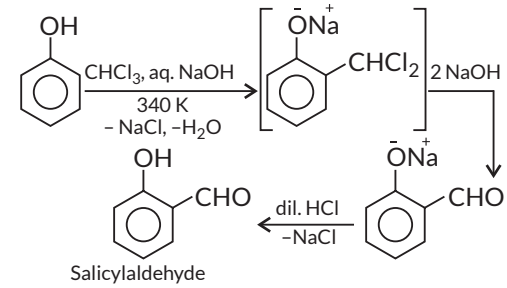
o-Nitrophenol
(Intramolecular H-bonding)



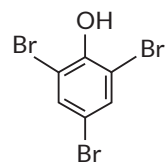
p-Nitrophenol
(Intermolecular H-bonding)

That's why, *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

35. **Reimer–Tiemann reaction :**



36. (i) $CH_3CH_2OH \xrightarrow{Cu/573K} CH_3CHO$

(ii) $C_6H_5OH \xrightarrow{Br_2(aq)}$ 

2,4,6 -Tribromophenol

37. (a) Phenol is more acidic than cyclohexanol due to resonance effect or delocalisation of π-electrons in benzene which stabilises the negative charge present on O-atom while in cyclohexanol, alkyl group is present which shows +*I* effect that destabilises the negative charge and hence, removal of H-atom becomes difficult.
(b) Phenol gives violet colour with neutral $FeCl_3$ solution while cyclohexanol does not.

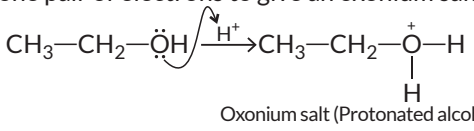
38. (i) Phenol is a stronger acid than an alcohol due to the stabilisation of phenoxide ion through resonance. Due to higher electronegativity of sp^2 hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of O–H

bond and results in an increase in ionisation of phenol than that of alcohol. Thus, removal of proton is easier in case of phenol as compared to alcohol.

(ii) The boiling point of alcohol decreases with increase in branching of alkyl chain due to a decrease in surface area. The decrease in surface area decreases the van der Waals forces of attraction causing a decrease in the boiling point.

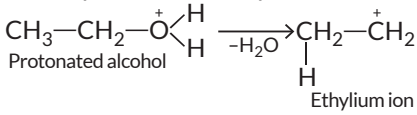
OR

(i) **Mechanism of dehydration :** The H^+ ion of acid acts as electrophile and attacks at the oxygen atom of alcohol having lone pair of electrons to give an oxonium salt.



Oxonium salt (Protonated alcohol)

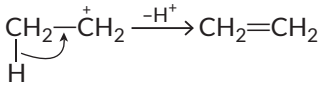
Water is removed from protonated salt to give carbocation (ethylium ion). As formation of intermediate is a slow step, hence this step is rate determining step.



Protonated alcohol

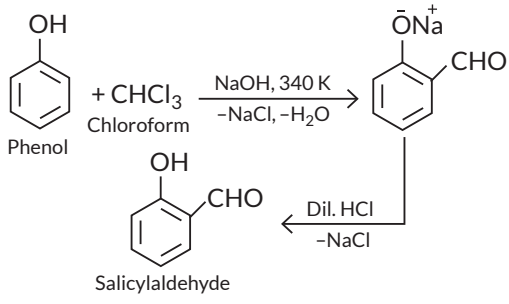
Ethylium ion

As ethylium ion (carbocation) is highly reactive species, it will try to be stabilized as soon as possible by the removal of proton to give alkene. This is a fast step.

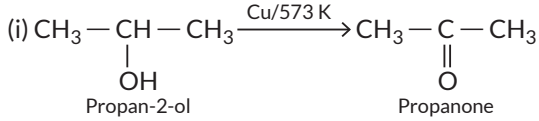


The carbocation is formed as intermediate, so rearrangement of carbocation is also possible which gives rise to more than one products. The major product will be according to Saytzeff rule.

(ii)



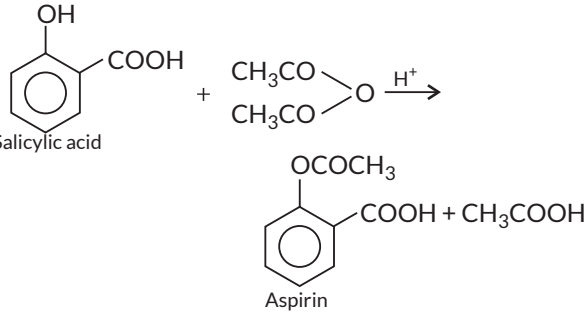
39. (i)



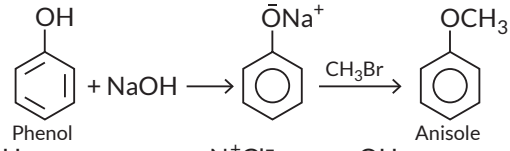
Propan-2-ol

Propanone

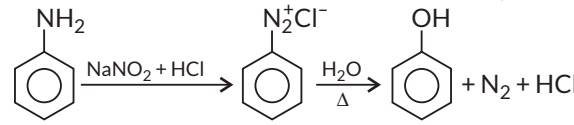
(ii)



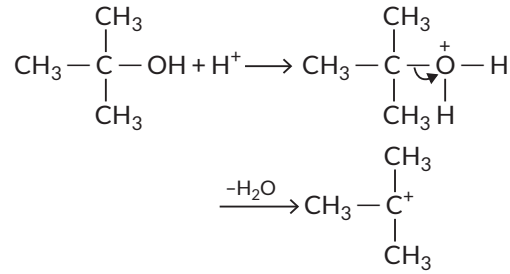
40. (i)



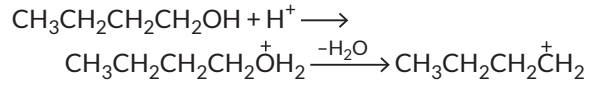
(ii)



41. Acid catalysed dehydration of alcohols follows carbocation mechanism.



3° carbocation (more stable)



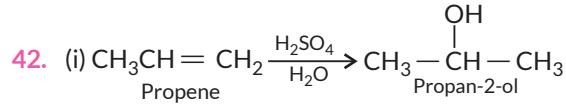
1° carbocation (less stable)

Hence, dehydration of *tert*-butanol (which forms 3° carbocation) is faster than *n*-butanol (which forms primary carbocation).

Answer Tips

➲ The relative ease of dehydration of alcohols follows the order : 3° > 2° > 1°.

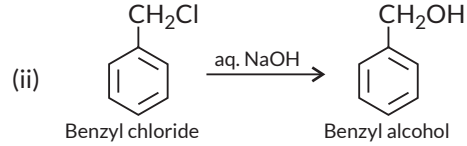
42. (i)



Propene

Propan-2-ol

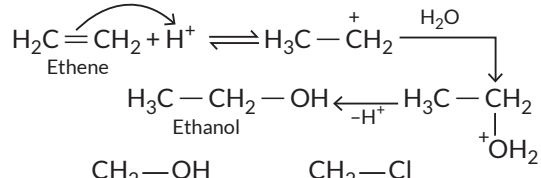
(ii)



Benzyl chloride

Benzyl alcohol

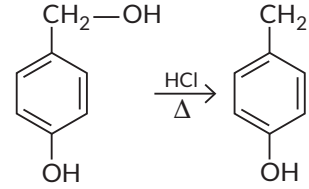
43.



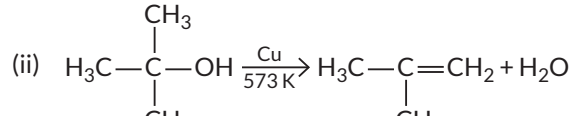
Ethene

Ethanol

44. (i)



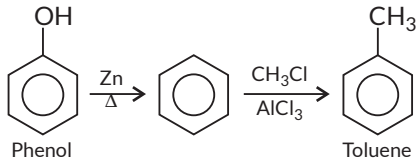
(ii)



2-Methylpropan-2-ol

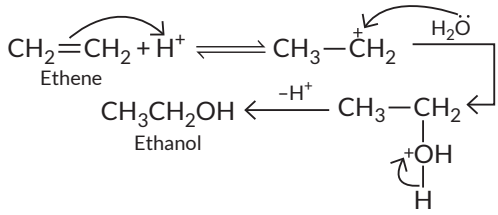
2-Methylpropene

45. (a)



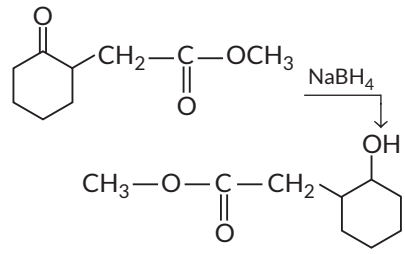
(b) $CH_3CH_2OH \xrightarrow[\text{or PCC}]{CrO_3} CH_3CHO$
Ethanol → Ethanal

46. (a)

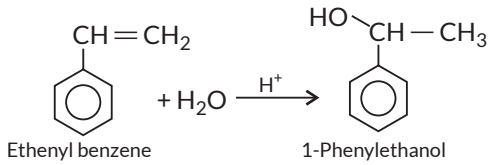


(b) IUPAC name of the given compound:
2, 6-dimethyl phenol

47. (i)

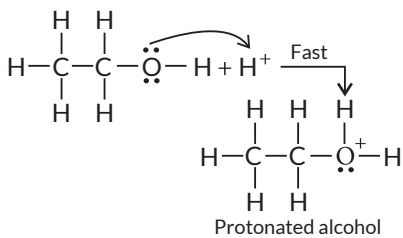


(ii)

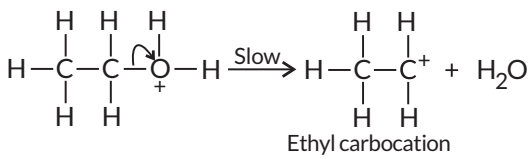


48. Acid catalysed dehydration of alcohols at high temperature takes place with formation of a carbocation.
Mechanism : The dehydration of ethanol involves the following steps :

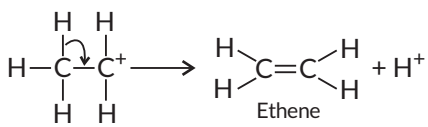
I. Formation of protonated alcohol.



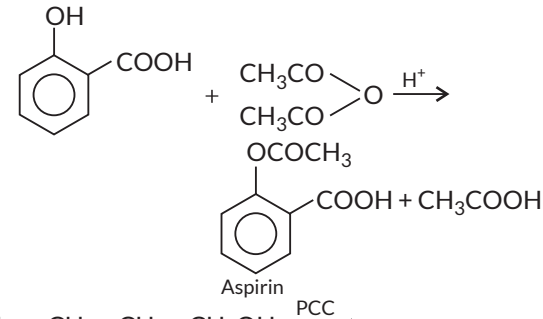
II. Formation of carbocation.



III. Formation of ethene by elimination of a proton.



49. (i)



(ii) $CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$
But-2-en-1-ol → But-2-enal

Answer Tips
➲ PCC is an oxidising agent, oxidises 1° and 2° alcohols to aldehyde and ketone respectively.

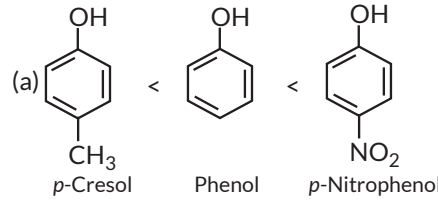
50. (i) Distinction between ethanol and phenol can be done by $FeCl_3$ test. Phenol gives a violet colouration with $FeCl_3$ solution while ethanol does not.

$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(C_6H_5O)_6]^{3-} + 3H^+ + 3HCl$
Phenol → Violet colouration

$C_2H_5OH + FeCl_3 \longrightarrow$ No violet colouration

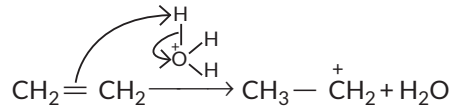
(ii) Propanol (1° alcohol) and 2-methylpropan-2-ol (3° alcohol) can be distinguished by Lucas test. With Lucas reagent (conc. HCl and anhyd. $ZnCl_2$), 1° alcohols show no cloudiness while 3° alcohols show cloudiness immediately.

51. (a)



Answer Tips
➲ Electron donating groups at *p*-position decrease acidity while electron withdrawing groups increase acidity.

(b)



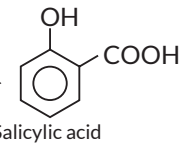
52. (a) $CH_3-\underset{\text{Butan-2-ol}}{\underset{|}{\overset{OH}{CH}}}-CH_2-CH_3 \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$
Butan-2-one

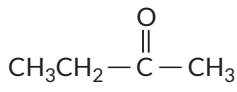
(b) $CH_3-\underset{\text{Butan-2-ol}}{\underset{|}{\overset{OH}{CH}}}-CH_2-CH_3 \xrightarrow{SOCl_2} \underset{\text{2-Chlorobutane}}{\underset{|}{\overset{Cl}{CH}}}-CH_2-CH_3$

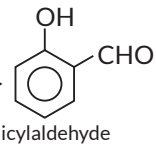
53. (i) $CH_3-CH=CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$

Answer Tips

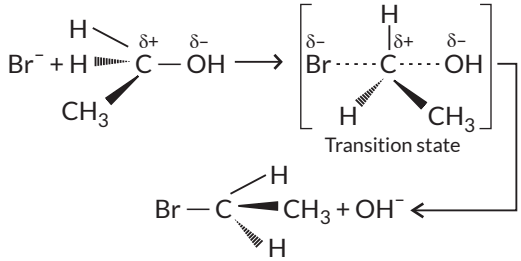
- Hydroboration–oxidation of alkene takes place as addition of water to alkene in anti-Markovnikov's manner.

(ii) $C_6H_5OH \xrightarrow[(ii)\ CO_2,\ H^+]{(i)\ aq.\ NaOH}$  Salicylic acid

54. (i) $CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573\ K}$  Butan-2-one

(ii) $C_6H_5-OH \xrightarrow[(i)\ H^+]{(i)\ CHCl_3 + aq.\ NaOH}$  Salicylaldehyde

55. The reaction proceeds through nucleophilic substitution bimolecular (S_N2) mechanism, as shown below :

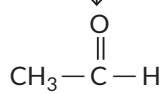


Inversion of configuration takes place during the reaction.

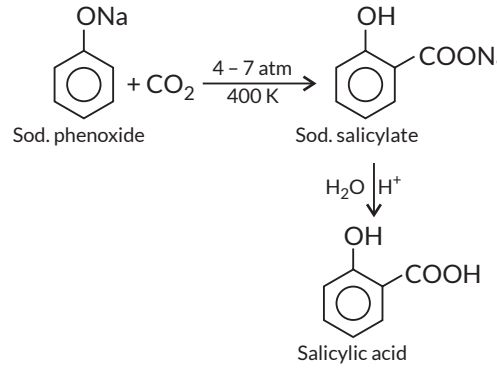
56. (i) Bromine water, ($Br_{2(aq)}$)
(ii) Lithium aluminium hydride, ($LiAlH_4$) or H_2/Ni
(iii) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and $AlCl_{3(anhy.)}$
(iv) Acidified potassium permangante, $KMnO_4$ and H_3O^+

57. (i) Zinc dust
(ii) Concentrated H_2SO_4
(iii) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and $AlCl_3$ (anhy.)
(iv) Cu at 573 K

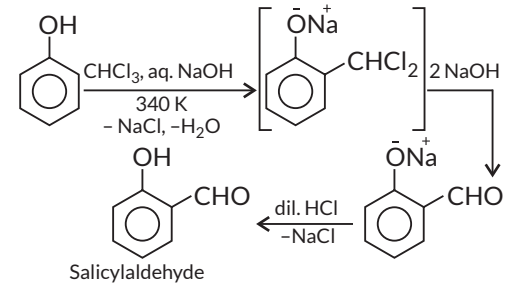
58. (i) $\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[H_2O]{H_2SO_4} \underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$

(ii) $\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + KOH_{(aq)} \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[573\ K]{Cu}$  Ethanal

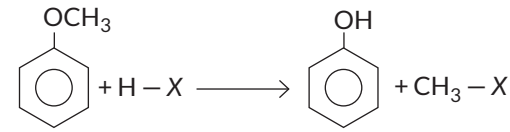
59. (i) **Kolbe's reaction :** When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



(ii) **Reimer–Tiemann reaction :**

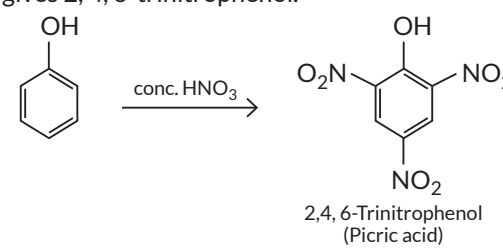


60. (i) Due to resonance, C—O bond acquires some partial double bond character. So, in phenol, C—O bond length is smaller than methanol.
(ii) Butanol > Butanal > Ethoxyethane > *n*-Butane
(117.7°C) (74.8°C) (34.6°C) (–1°C)
The boiling point of alcohol is higher in comparison to hydrocarbons and ethers of comparable molecular masses due to intermolecular hydrogen bonding.
The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
The boiling point of ether is higher than alkanes of comparable molecular masses but is much lower than that of alcohols.

(iii) 

Alkyl aryl ethers reaction with H*X* results in the cleavage of *R*—O bond instead of Ar—O bond as Ar—O bond is more stable due to double bond character.

61. (a) Phenol when treated with concentrated nitric acid gives 2, 4, 6-trinitrophenol.



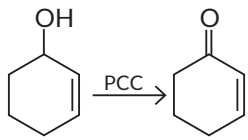
(b) $CH_3MgBr + CH_3COCH_3 \longrightarrow BrMg{-}O{-}C(CH_3)_3$ (Propanone)

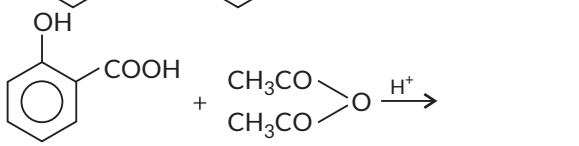
$\xrightarrow{H_2O}$

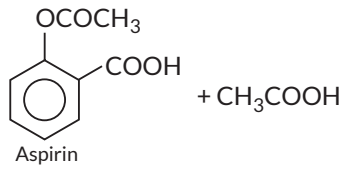
$HO{-}C(CH_3)_3 + Mg(OH)Br$ (2-Methylpropan-2-ol)

(c) Phenol $\xrightarrow{+NaOH}$ $\xrightarrow{CH_3Br}$ Anisole

(d) $CH_3{-}CH{=}CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} CH_3CH_2CH_2OH$ (Propene → Propan-1-ol)

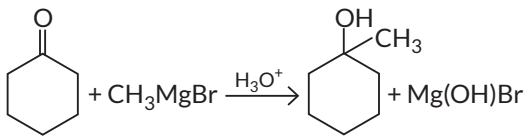
62. (i) 

(ii) 

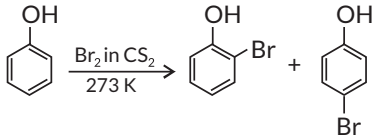


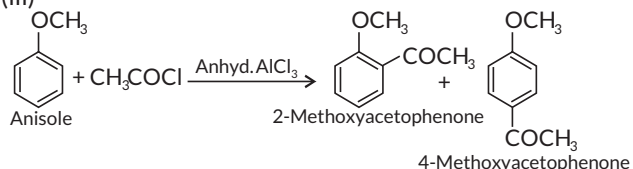
Aspirin

$+ CH_3COOH$

(iii) 

63. (i) $CH_3CH_2OCH_3 + HI \rightarrow CH_3CH_2OH + CH_3I$

(ii) 

(iii) 

Anisole → 2-Methoxyacetophenone + 4-Methoxyacetophenone

64. Test to distinguish between:

(a) **Phenol and 1-propanol :** Phenols react with neutral $FeCl_3$ solution to give blue, violet or green colouration whereas alcohols do not react with neutral $FeCl_3$ solution.

(b) **Ethanol and dimethyl ether :** When ethanol is heated with iodine and aqueous NaOH solution at 333-343 K, a yellow ppt. of iodoform is produced. Dimethyl ether do not undergo this test

$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O$

(c) **1-propanol and 2-methyl-2-propanol :** When 2-methyl-2-propanol (3° alcohol) is treated with Lucas reagent at room temperature, turbidity appears immediately. 1-propanol (1° alcohol) does not react with Lucas reagent at room temperature, hence no turbidity is formed.

65. (a) $HCHO + (CH_3)_2CHMgBr \longrightarrow CH_3{-}CH(CH_3){-}CH_2{-}O\bar{M}gBr^+ \xrightarrow{H_3O^+} CH_3{-}CH(CH_3){-}CH_2OH$

(b) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

$H{-}\ddot{O}{-}H + H^+ \rightleftharpoons H{-}\overset{+}{\underset{H}{O}}{-}H$

$CH_2{=}CH_2 \xrightarrow{H_2O^+H} CH_3{-}CH_2^+ + H_2\ddot{O}: \xrightarrow{-H^+} CH_3{-}CH_2{-}OH$

66. (a) (i) Phenol $\xrightarrow[\text{Oxidation}]{Na_2Cr_2O_7/H_2SO_4}$ Benzoquinone

(ii) $CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + CH_3MgBr \longrightarrow CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O\bar{M}gBr^+$

$\xrightarrow{H_2O}$ $Mg(OH)Br + CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH$

(b) Propanol has higher boiling point than butane due to presence of intramolecular H-bonding.

67. (i) Phenol to anisole

Phenol $\xrightarrow{+NaOH}$ $\xrightarrow{CH_3Br}$ Anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

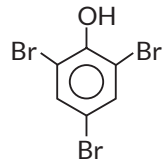
$CH_3{-}CH(OH){-}CH_3 \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3$ (Propan-2-ol)

$\xrightarrow[(ii)\ H^+/H_2O]{(i)\ CH_3MgBr}$ $CH_3{-}\underset{CH_3}{\overset{OH}{C}}{-}CH_3$ (2-Methylpropan-2-ol)

(iii) Aniline to phenol

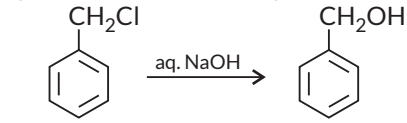
Aniline $\xrightarrow{NaNO_2 + HCl}$ $\xrightarrow[\Delta]{H_2O}$ Phenol $+ N_2 + HCl$

68. (i) $CH_3{-}CH{=}CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} CH_3CH_2CH_2OH$

(ii) $C_6H_5OH \xrightarrow{Br_2(aq)}$ 

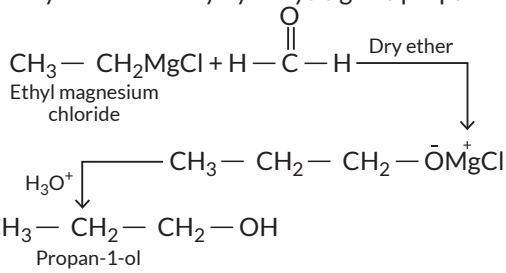
2,4,6-Tribromophenol

(iii) $CH_3CH_2OH \xrightarrow{Cu/573\ K} CH_3CHO$

69. (i) 

Benzyl chloride — Benzyl alcohol

(ii) Ethyl magnesium chloride on addition to formaldehyde followed by hydrolysis gives propan-1-ol.



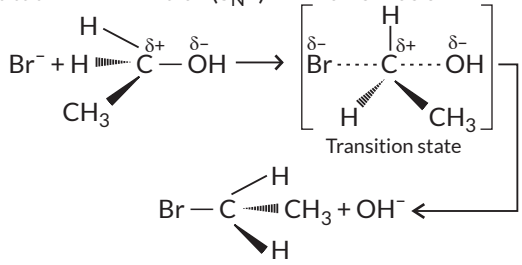
Ethyl magnesium chloride

Propan-1-ol

(iii) $CH_3CH{=}CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3{-}CH(OH){-}CH_3$

Propene — Propan-2-ol

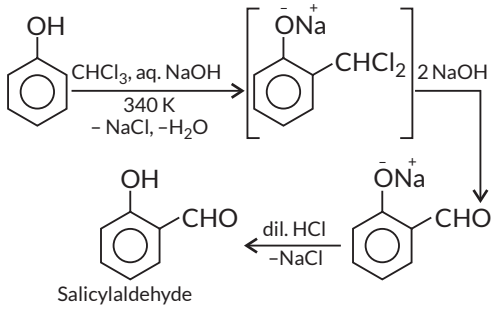
70. (a) The reaction proceeds through nucleophilic substitution bimolecular (S_N2) mechanism as shown below :



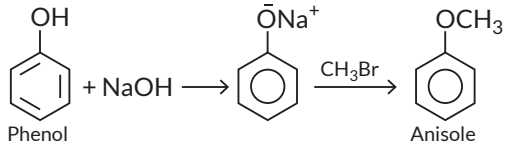
Transition state

Inversion of configuration takes place during this reaction.

(b) Reimer–Tiemann reaction :



Salicylaldehyde

71. (a) (i) 

Phenol — Anisole

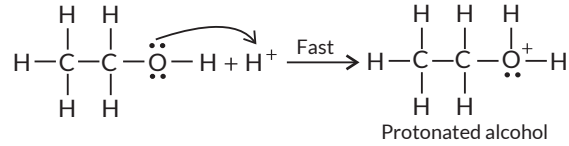
(ii) $CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow[H_2O]{CH_3MgBr} CH_3CH(OH)CH_3$

Ethanol — Propan-2-ol

(b) Acid catalysed dehydration of alcohols at high temperature takes place with formation of a carbocation.

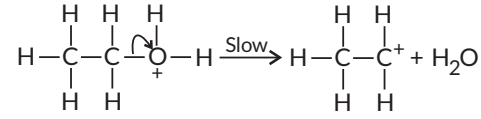
Mechanism : The dehydration of ethanol involves the following steps :

Step I : Formation of protonated alcohol.



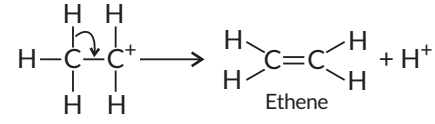
Protonated alcohol

Step II : Formation of carbocation.



Ethyl carbocation

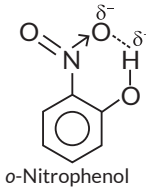
Step III : Formation of ethene by elimination of a proton.



Ethene

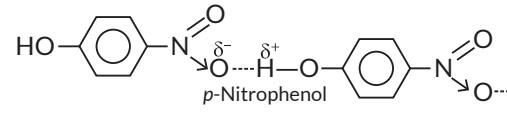
(c) Phenol undergoes electrophilic substitution reaction more easily than benzene due to strong ring activating effect of –OH group attached to benzene ring.

72. (a) (i) *o*-Nitrophenol is more volatile than *p*-nitrophenol due to the presence of intramolecular H-bonding. *p*-Nitrophenol shows intermolecular H–bonding.



o-Nitrophenol

(Intramolecular H-bonding)

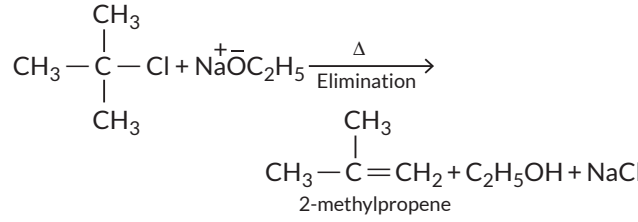


p-Nitrophenol

(Intermolecular H-bonding)

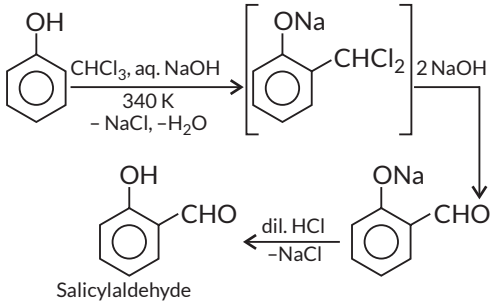
That's why *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

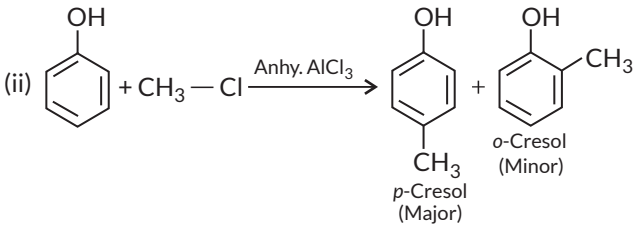
(ii) This is because *tert*-alkyl halides undergo elimination instead of substitution.



2-methylpropene

(b) (i) Reimer–Tiemann reaction :



(ii) 

(c) Distinction between ethanol and phenol can be done by $FeCl_3$ test. Phenol gives a violet colouration with $FeCl_3$ solution while ethanol does not.

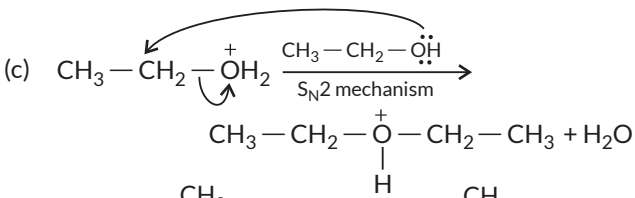
$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{[Fe(C_6H_5O)_6]^{3-}} + 3H^+ + 3HCl$$

$$C_2H_5OH + FeCl_3 \longrightarrow \text{No violet colouration}$$

73. (a) (i) Br_2/H_2O (ii) BH_3 in $THF/H_2O_2, OH^-$

(b) (i) Ethanol < phenol < *p*-nitrophenol

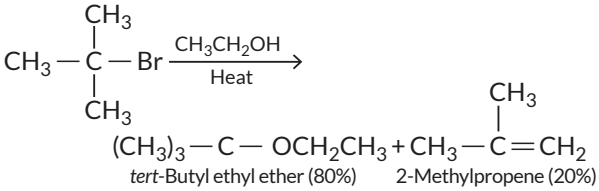
(ii) Propane < propanal < propanol

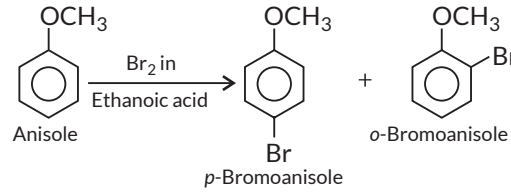
(c) 

74. (a) : $CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-OCH_3 + HI \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-I + CH_3OH$

75. (d): In ether, the C—O—C bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky(-*R*) groups.

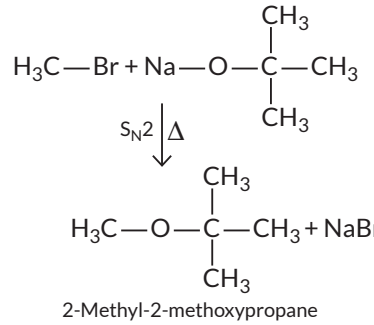
76. The given conversion is not possible by treating sodium ethoxide with *t*-butyl chloride or bromide since, under these conditions an alkene *i.e.*, isobutylene (2-methylpropene) will be the main product. If however, *t*-butyl bromide is heated with a weak nucleophile such as pure ethanol both substitution and elimination occur in which substitution product predominates. Thus,

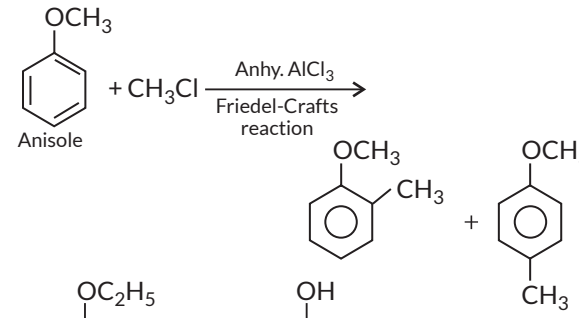


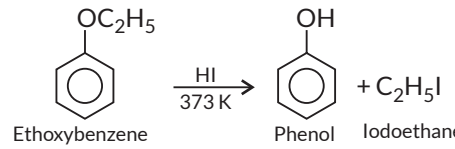
77. 

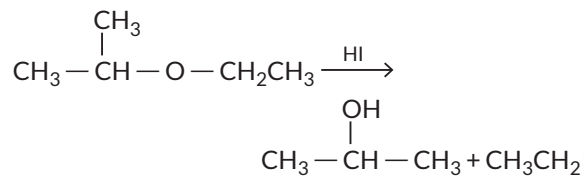
Concept Applied

➲ $-OCH_3$ group is *o/p* directing group.

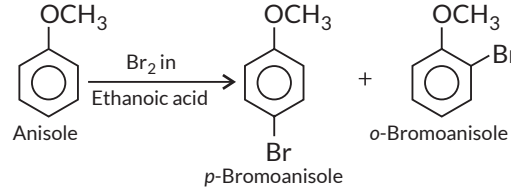
78. 

79. 

80. 

81. 

82. $CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-OCH_3 + HI \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-I + CH_3OH$

83. 

84. **Williamson ether synthesis :** Alkyl halide when treated with sodium alkoxide gives dialkyl ether.

$$C_2H_5ONa + C_2H_5Cl \longrightarrow C_2H_5 — O — C_2H_5 + NaCl$$

85. **Mechanism :** The formation of ether is nucleophilic bimolecular reaction.

Step I : $CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H$

Step II : $CH_3-CH_2-\ddot{O}-H + CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H \xrightarrow{-H_2O} CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-CH_2-CH_3$

Step III : $CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-CH_2-CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3 + H^+$

86. $CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)-Br + \overset{+}{Na}\bar{O}CH_3 \xrightarrow[\text{Elimination}]{\Delta} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3OH + NaBr$

2-methyl propene

87. (i) Ethanol has higher boiling point because of strong intermolecular hydrogen bonding whereas in methoxymethane, molecules are held by dipole-dipole interaction.

(ii) When the alkyl group is a tertiary group, the halide formed is tertiary halide. The departure of leaving group $-\overset{+}{\underset{H}{O}}-CH_3$ creates a more stable carbocation (3°) and the reaction follows S_N1 mechanism.

$$CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)-\overset{+}{O}(H)-CH_3 \xrightarrow{\text{Slow}} CH_3-\overset{CH_3}{\overset{|}{C}}{}^{+}(CH_3) + CH_3OH$$

$$CH_3-\overset{CH_3}{\overset{|}{C}}{}^{+}(CH_3) + I^- \xrightarrow{\text{Fast}} CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)-I$$

88. (i) **Mechanism :** The formation of ether is nucleophilic bimolecular reaction.

Step I : $CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H$

Step II : $CH_3-CH_2-\ddot{O}-H + CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-H \xrightarrow{-H_2O} CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-CH_2-CH_3$

Step III : $CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{O}}}-CH_2-CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3 + H^+$

(ii) **Hydroboration-oxidation reaction :** Diborane (B_2H_6) adds on alkane to give trialkyl boranes which on oxidation with hydrogen peroxide in presence of alkali give alcohols.

$$CH_3CH=CH_2 + (H\text{-}BH_2)_2 \longrightarrow CH_3-CH(H)-CH_2-BH_2$$

$$CH_3-CH(H)-CH_2-BH_2 \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2BH \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_3B$$

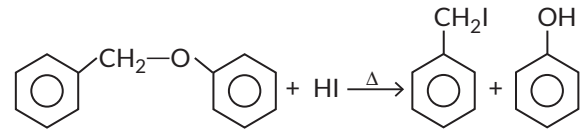
$$(CH_3CH_2CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 3CH_3CH_2CH_2OH + B(OH)_3$$

Propan-1-ol

89. (i) $3CH_3-CH=CH_2 \xrightarrow[H_2O_2/OH^-]{(BH_3)_2} 3CH_3-CH_2-CH_2-OH$

Propanol

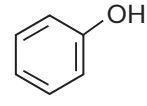
(ii) $CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} H_3C-\overset{CH_3}{\overset{|}{C}}=CH_2$

(iii) 

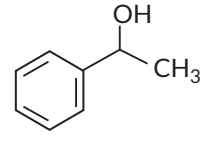
CBSE Sample Questions

1. **(a) :** (i) $CH_3CH_2CH(OH)CH_3$ (secondary alcohol)

(ii) $(C_2H_5)_3COH$ (tertiary alcohol)

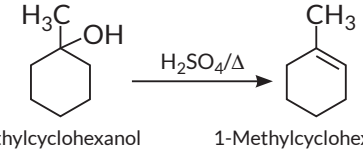
(iii) 

(phenol, not an alcohol)

(iv) 

(secondary alcohol) **(0.77)**

2. **(b):**



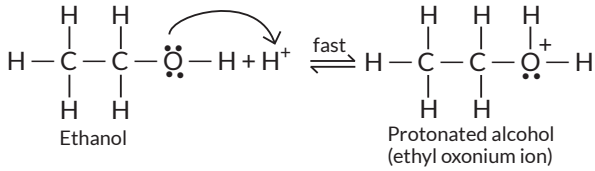
1-Methylcyclohexanol 1-Methylcyclohexene

According to Saytzeff rule, highly substituted alkene is major product. Here, dehydration reaction takes place, alkene is formed due to the removal of a water molecule. **(1)**

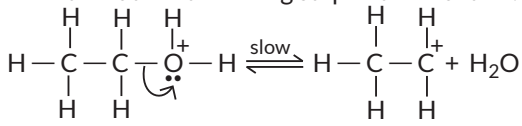
3. **(a):** Alcohols form intermolecular hydrogen bonds. So, alcohols have higher boiling points than hydrocarbons of comparable masses. **(0.77)**

4. **(a):** Protonation of alcohol molecule is initial step in dehydration of alcohols to alkenes.

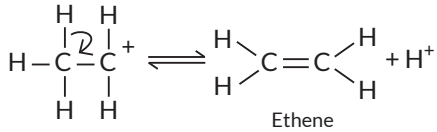
Step 1 : Formation of protonated alcohol



Step 2 : Formation of carbocation : It is the slowest step and hence the rate determining step of the reaction.

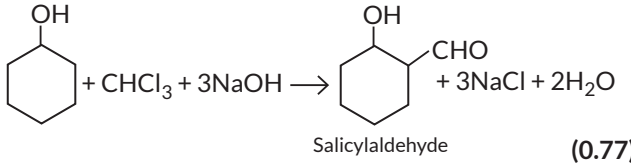


Step 3 : Formation of ethene by elimination of a proton.



(0.77)

5. (c) : Reimer-Tiemann reaction is used to prepare salicylaldehyde, Kolbe's reaction to prepare salicylic acid, Etard reaction for benzaldehyde and Stephen's reduction for aldehyde.

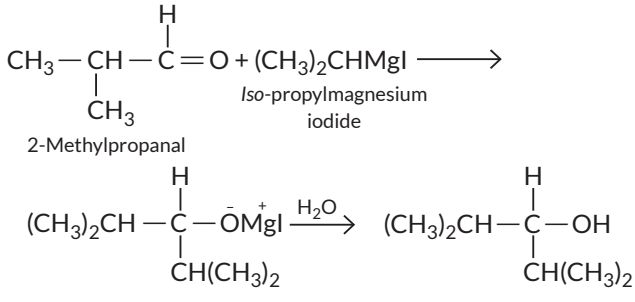


(0.77)

6. (c) : Lower molecular mass alcohols are able to form hydrogen bonds with water. Hence, they are miscible in water in all proportions. **(0.77)**

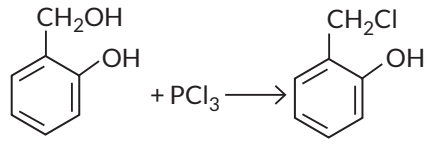
7. (b): Phenol does not undergo nucleophilic substituiton reaction easily due to partial double bond character of C – OH bond. **(0.77)**

8. (d): 2-Methylpropanal and *iso*-propyl magnesium iodide react to form 2,4-dimethylpentane 3-ol.



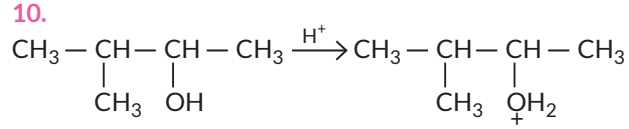
(0.77)

9. (b): 2-(Chloromethyl) phenol is formed.

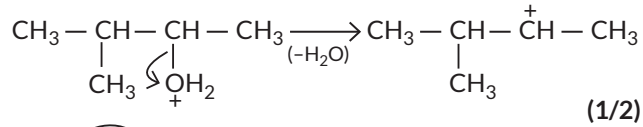


(0.77)

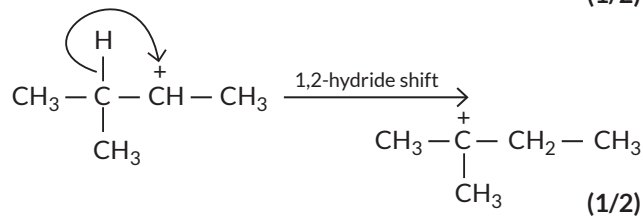
10.



(1/2)



(1/2)



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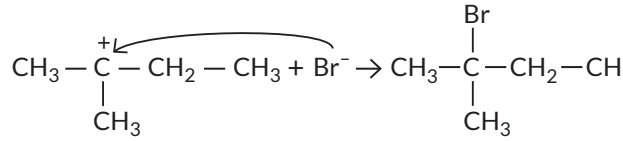


(1/2)

11. (d): $C_6H_5CH_2OC_6H_5 + H^+ \longrightarrow C_6H_5CH_2\overset{+}{O}HC_6H_5 \xrightarrow{Br^-} C_6H_5CH_2Br + C_6H_5OH$ (A) (B) **(1)**

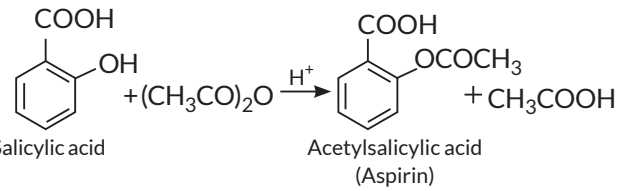
12. (b): As hydrogen bonding does not exist among ether molecule, it is more volatile than alcohol. **(1)**

13. (c) : It is S_N2 reaction.
In this, alkoxide ion reacts with primary alkyl halide in a single step to form ether.)

$$CH_3Br \xrightarrow{CH_3O^-Na^+} CH_3OCH_3 + NaBr$$ **(0.77)**

14. (a): $CH_3CH_2OCH_3 + HI \rightarrow CH_3CH_2OH + CH_3I$ **(1)**

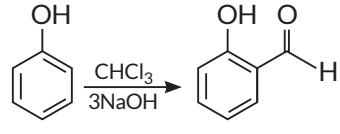
15. (a) : Aspirin is formed.



(1)

(b) $(CH_3)_3CCl \xrightarrow{\text{Sodium ethoxide}} (CH_3)_2C=CH_2$ 2-Methylpropene **(1)**

(c) *o*-hydroxybenzaldehyde will be formed.



(1)

Self Assessment

Case Based Questions (5 marks)

1. **Read the passage given below and answer the following questions :**
A compound (*X*) containing C, H and O is unreactive towards sodium. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (*X*) yields only one organic product (*Y*). On hydrolysis, (*Y*) yields a new compound (*Z*) which can be converted into (*Y*) by reaction with red phosphorus and iodine. The compound (*Z*) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.
(i) The compound (*X*) is an
(a) acid (b) aldehyde
(c) alcohol (d) ether.
(ii) The IUPAC name of the acid formed is
(a) methanoic acid (b) ethanoic acid
(c) propanoic acid (d) butanoic acid.
(iii) Compound (*Y*) is
(a) ethyl iodide (b) methyl iodide
(c) propyl iodide (d) mixture of (a) and (b).
(iv) Compound (*Z*) is
(a) methanol (b) ethanol
(c) propanol (d) butanol.
(v) Compound (*X*) on treatment with excess of Cl_2 in presence of light gives
(a) α-chlorodiethyl ether
(b) α, α'-dichlorodiethyl ether
(c) perchlorodiethyl ether
(d) none of these.

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

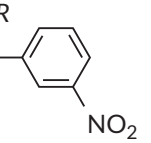
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

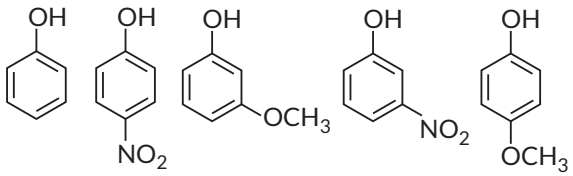
2. **Assertion :** CH_3OCH_3 and C_2H_5OH has comparable molecular weight but boiling point of C_2H_5OH is more than dimethyl ether.
Reason : C_2H_5OH forms intermolecular H-bonding while CH_3OCH_3 forms intramolecular H-bonding.

3. **Assertion :** *tert*-Butyl alcohol undergoes acid catalysed dehydration readily than propanol.
Reason : 2° Alcohols give blue colour for Victor-Meyer's test.

Multiple Choice Questions (1 mark)

4. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?
(a) 1 (b) 2 (c) 3 (d) 4

5. Which of the following species can act as the strongest base?
(a) ^-OH (b) ^-OR
(c) $^-C_6H_5$ (d) 

6. Mark the correct order of decreasing acid strength of the following compounds.

(I) (II) (III) (IV) (V)
(a) V > IV > II > I > III (b) II > IV > III > I > V
(c) IV > V > III > II > I (d) V > IV > III > II > I

7. The process of converting alkyl halides into alcohols involves_____.
(a) addition reaction
(b) substitution reaction
(c) dehydrohalogenation reaction
(d) rearrangement reaction

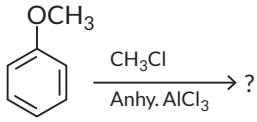
VSA Type Questions (1 mark)

8. Which type of alcohol is formed by hydroboration oxidation of unsymmetrical alkene?
9. What is Lucas reagent?
10. What happens when 3° alcohol is treated with $KMnO_4$ at high temperature?
11. What is esterification?

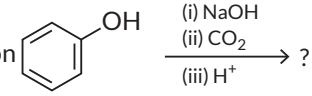
SA I Type Questions (2 marks)

12. Anisole undergoes bromination with bromine and ethanoic acid even in absence of iron bromide catalyst. Why?
13. Why are aromatic ethers *o* and *p*-directing?
14. Alcohols act as Bronsted acid and Bronsted base both. Explain.

15. Write the major product in the following reaction :

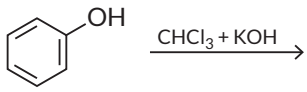


16. Complete the reaction



OR

Predict the product of the following reaction:



SA II Type Questions (3 marks)

17. What happens when *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH?

18. How will you obtain 1-propanol from 2-propanol (in three steps)?

19. Provide a suitable explanation for the observation that when anisole reacts with HI, it results in the formation of CH_3I and not C_6H_5I.

20. How can the following conversions be carried out?
    (i) Butene to butan-2-ol.
    (ii) Anisole to phenol.

    OR

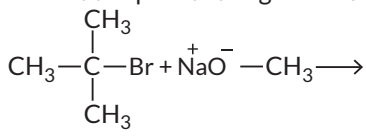
    What happens when C_2H_5OH is treated with conc. H_2SO_4 at 443 K? Explain the mechanism of this reaction.

Case Based Questions (4 marks)

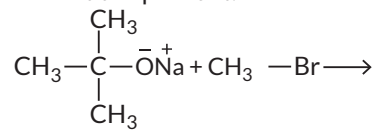
21. **Read the passage given below and answer the following questions :**

Williamson's synthesis is used for the preparation of symmetrical as well as unsymmerical ether. It is S_N2 reaction mechanism. In Williamson's synthesis, 1° alkyl halides are used for preparation of ethers because 2° and 3° alkyl halides give alkene. Ethers are cleaved by hydrogen halides to alcohol and alkyl halide where alkyl halide is corresponding to that alkyl which has less number of carbon atom (it is because of less steric hindrance). In polar media unsymmetrical ether like tertiary butyl ethyl ether gives ethyl alcohol and tertiary butyl halide as reaction proceeds *via* carbocation intermediate.

(i) Predict the product of given reaction.



(ii) Predict the product.



(iii) Why is Williamson's synthesis not applicable to tertiary halides?

OR

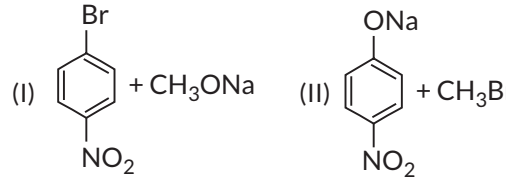
Write the names of reagents and equations for the preparation of Ethoxybenzene by Williamson's synthesis.

LA Type Questions (5 marks)

22. (i) Write the distinction test for ethyl alcohol and 2-propanol.
    (ii) Of the two hydroxy organic compounds *R*OH and *R'*OH, the first one reacts with acids and the other one reacts with bases to give salt. How is *R* different from *R'*?

23. (i) What is absolute alcohol?
    (ii) Arrange the following sets of compounds in order of their increasing boiling points.
    Pentan-1-ol, *n*-butane, pentanal, ethoxyethane.
    (iii) Explain how an –OH group attached to a carbon in the benzene ring activates benzene towards electrophilic substitution.

24. (a) How will you prepare picric acid from phenol?
    (b) (i) Which of the following is an appropriate set of reactants for preparation of 1-methoxy-4 nitrobenzene and why?



    (ii) Illustrate with examples the limitations of Williamson's synthesis for the preparation of certain types of ethers.

25. (a) Upon treatment with sulphuric acid, a mixture of ethyl and *n*-propyl alcohols yield a mixture of three ethers. What are they?
    (b) A mixture of *tert*-butyl alcohol and ethyl alcohol gives a good yield of a single ether. What ether is this likely to be? How do you account for this good yield?

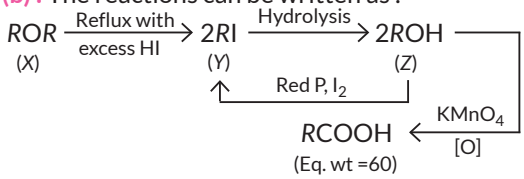
    OR

    (i) Between *o*-nitrophenol and *p*-nitrophenol, which one is steam volatile and why?
    (ii) The C—O bond length in phenol is less than that in methanol. Why?
    (iii) What happens when dialkyl ether is heated with excess of hydrogen halide?

Detailed SOLUTIONS

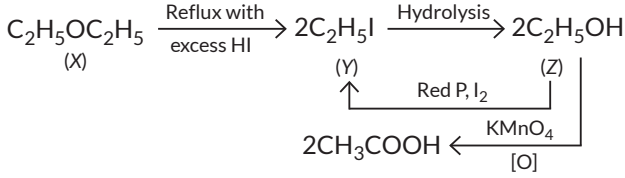
1. (i) (d) : Since the compound *X* is unreactive towards sodium so it is neither an acid nor an alcohol.
Since the compound *X* is unreactive towards Schiff's base so it is not an aldehyde.
The compound *X* forms only one product on reaction with excess HI, indicates that the compound *X* is an ether.

(ii) (b) : The reactions can be written as :



Since, the equivalent weight of carboxylic acid is 60, so it must be CH_3COOH *i.e.*, ethanoic acid.

(iii) (a): The alcohol *Z* in that case should be C_2H_5OH and the compound *Y* should be ethyl iodide.
X is therefore diethyl ether ($C_2H_5—O—C_2H_5$)



(iv) (b)

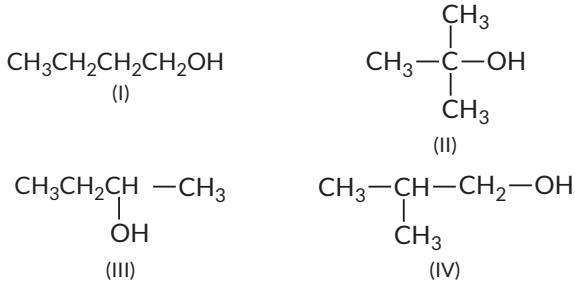
(v) (c): In the presence of light and excess of chlorine, all the hydrogen atoms of diethyl ether are substituted to give perchlorodiethyl ether.

$$\underset{\text{Diethyl ether}}{CH_3CH_2—O—CH_2CH_3} + \underset{\text{(excess)}}{10Cl_2} \xrightarrow{h\upsilon} \underset{\text{Perchlorodiethyl ether}}{CCl_3CCl_2—O—CCl_2—CCl_3} + 10HCl$$

2. (c): Due to the presence of hydroxyl group (–OH), there is extensive hydrogen bonding between the ethanol molecules (C_2H_5OH). But there is no such hydrogen bonding in dimethyl ether (due to absence of –OH group). So, boiling point of dimethyl ether is much lower than ethanol.

3. (b): Alcohol which forms the more stable carbocation undergoes dehydration more readily. Since *tert*-butyl alcohol forms more stable *tert*-butyl cation, therefore, it undergoes dehydration more readily than propanol. 2° alcohols give blue colour for Victor Meyer test.

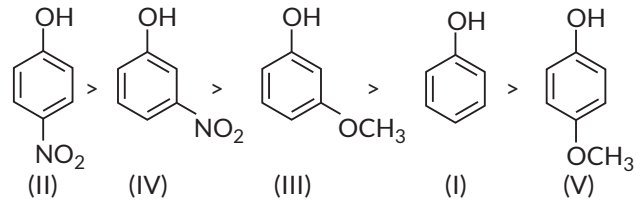
4. (a) : Only one alcohol of formula $C_4H_{10}O$ contains chiral carbon atom.



Only III is chiral in nature.

5. (b): ^-OR is the strongest base among given anions since, *R*(alkyl) group is an electron releasing group which increases electron density on O.

6. (b) :



$–NO_2$ is an electron withdrawing group which increases the acidity of phenol and the effect is more pronounced at *ortho* and *para*-positions. Whereas, methoxy group is an electron releasing group which decreases the acidity of phenol and the effect is more pronounced at *ortho* and *para*-positions, while at *meta*-position, *–I* effect of methoxy group is dominant which increases acidity of phenol comparatively.

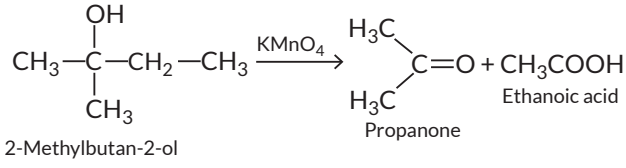
7. (b): Conversion of alkyl halides into alcohols involves substitution reaction.

$$RX \xrightarrow{NaOH} ROH + NaX$$

8. In case of hydroboration oxidation of alkene, the alcohol formed is (primary alcohol) opposite to Markownikoff's rule.

9. Conc. HCl and $ZnCl_2$ mixture is called Lucas reagent.

10. 3° alcohol reacts with $KMnO_4$ at high temperature to give carboxylic acid having lesser number of carbon atoms.

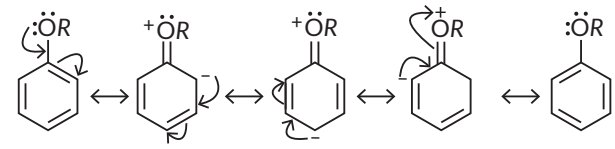


11. The formation of ester by the reaction of alcohol with carboxylic acid, acid chloride or acid anhydride is called esterification.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \longrightarrow \underset{\text{Ester}}{RCOOR'} + H_2O$$

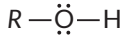
12. Anisole undergoes bromination with bromine and ethanoic acid even in absence of iron (III) bromide catalyst due to activation of benzene ring by the methoxy group through +*R*-effect.

13.



Due to presence of electron releasing group on benzene ring, electron density at *ortho* and *para*-positions increases. So, an electrophile easily attacks on it.

14. Due to presence of lone pair of electrons on oxygen atom, alcohols accept a proton which makes them Bronsted base and due to acidic hydogen, they donate the proton to strong base which makes them Bronsted acid.



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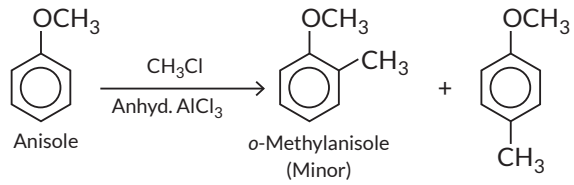

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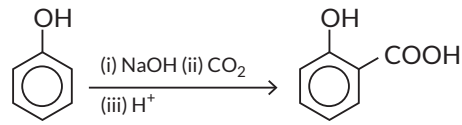
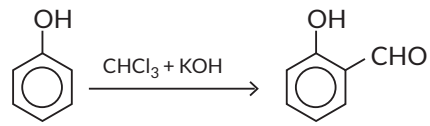
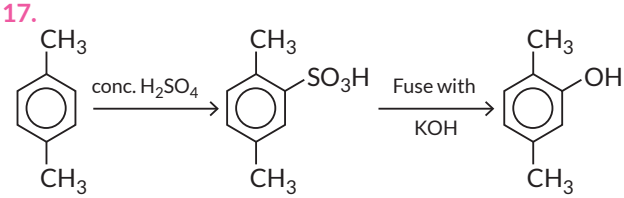


OR



17.



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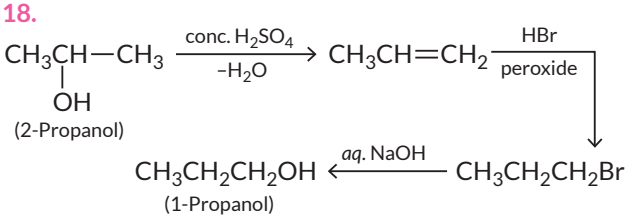
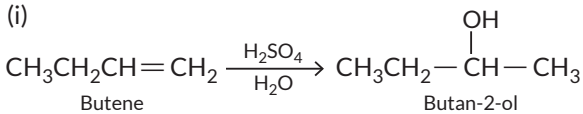


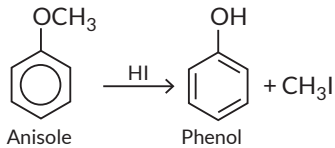
19. In case of anisole, methyl phenyl oxonium ion is formed *i.e.*, $C_6H_5-\overset{+}{O}(H)-CH_3$

The bond $O-CH_3$ is weaker than $O-C_6H_5$ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore, the attack of I^- ion breaks $O-CH_3$ bond, and CH_3I is formed instead of C_6H_5I.

20. (i)

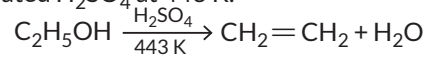


(ii)



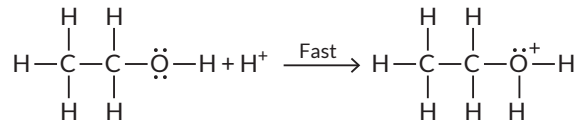
OR

Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.

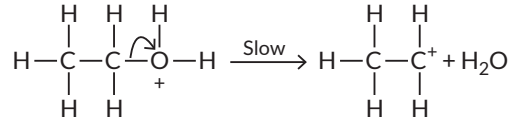


Mechanism : The dehydration of ethanol involves the following steps :

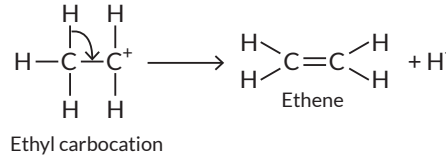
(i) **Formation of protonated alcohol :**



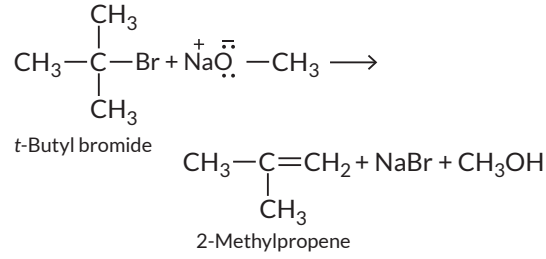
(ii) **Formation of carbocation :**



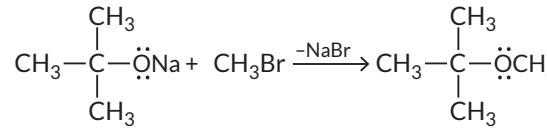
(iii) **Formation of ethene :**



21. (i)

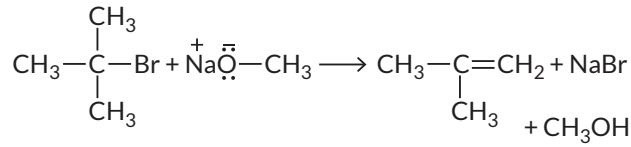


(ii)

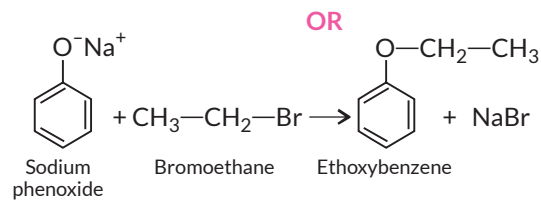


(iii) In case of secondary or tertiary alkyl halides, elimination competes over substitution and product formed is alkene.

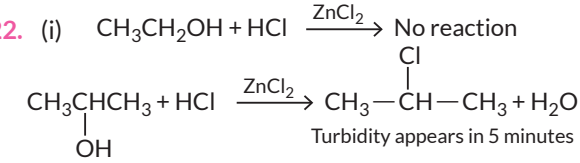
For example,



OR



22. (i)

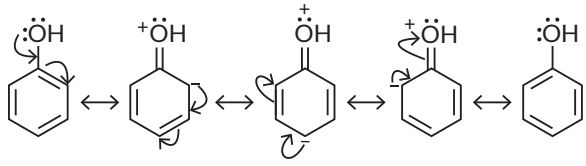


(ii) *R* is an alkyl group whereas *R′* is an aryl group.

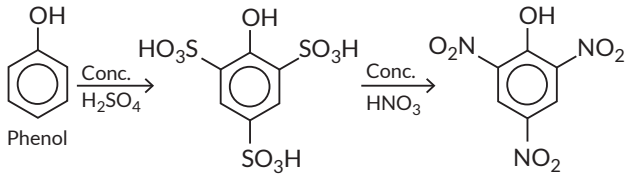
23. (i) Absolute alcohol is liquid alcohol that is at least 99% pure alcohol by weight.

(ii) *n*-butane < ethoxyethane < pentanal < pentan-1-ol

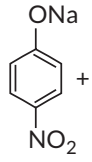
(iii) The —OH group when attached to benzene ring, activates it towards electrophilic substitution reaction by increasing the electron density on the benzene ring by releasing electrons due to mesomeric effect as shown below :



24. (a)



Phenol — Picric acid

(b) (i)  + CH_3Br is an appropriate set of reactants for the preparation for 1-methoxy-4-nitrobenzene because phenoxide ion can easily undergo S_N2 reaction with methyl bromide.

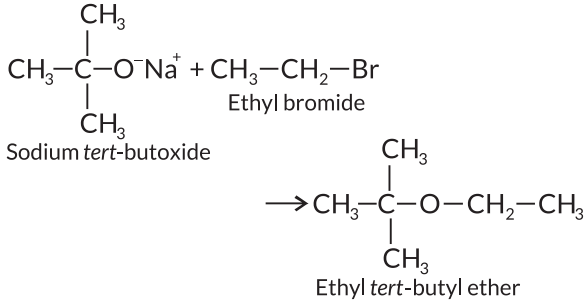
However —NO_2 present at *ortho* position decreases its nucleophilicity.

(ii) In Williamson's synthesis, an alkyl halide is treated with sodium or potassium salt of an alcohol or phenol to give ethers.

$$R—O^-Na^+ + R'—X \rightarrow R—O—R' + NaX$$

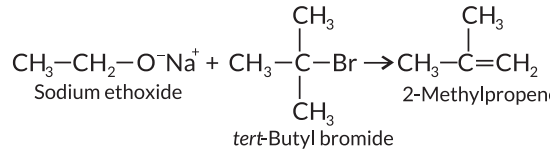
The reaction involves the nucleophilic substitution of the halogen atom by an alkoxide ion. For the preparation of aliphatic ethers by this method, the alkyl halides used should be primary because secondary or tertiary alkyl halides may undergo elimination to form alkenes due to strongly basic nature of alkoxides.

For example, if ethyl *tert*-butyl ether is to be prepared, then better yields are obtained by reactions of ethyl bromide with sodium *tert*-butoxide.



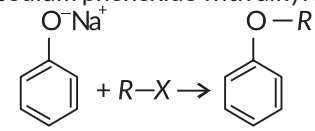
Sodium *tert*-butoxide — Ethyl bromide — Ethyl *tert*-butyl ether

But if the reaction between sodium ethoxide and *tert*-butyl bromide is carried out then 2-methylpropene is obtained as the major product.



Sodium ethoxide — *tert*-Butyl bromide — 2-Methylpropene

Another limitation is in the preparation of aliphatic-aromatic ethers where the reaction proceeds by the treatment of sodium phenoxide with alkyl halide.



25. (a) CH_3CH_2OH (ethyl alcohol) and $CH_3CH_2CH_2OH$ (*n*-propyl alcohol) by dehydration make a mixture of three ethers since each alcohol is 1° and follows S_N2 reaction.

$$CH_3CH_2OH + CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

Diethyl ether

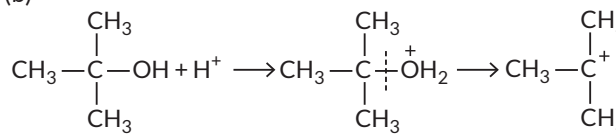
$$CH_3CH_2CH_2OH + CH_3CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2CH_2OCH_2CH_2CH_3 + H_2O$$

Dipropyl ether

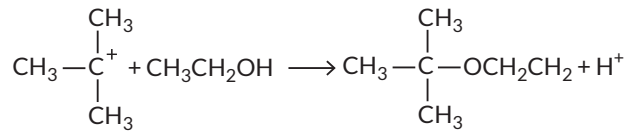
$$CH_3CH_2OH + CH_3CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2CH_2OCH_2CH_3 + H_2O$$

Ethyl propyl ether

(b)



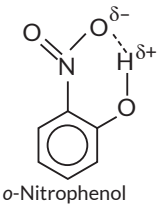
(3°) most stable carbocation



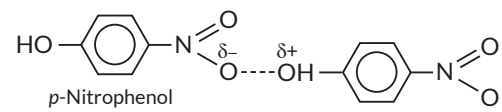
Since, protonated 3° alcohol (*tert*-butyl alcohol) can make most stable carbocation, hence this leads to the single ether in good quantity.

OR

(i) *o*-Nitrophenol is steam volatile due to intramolecular H–bonding. *p*-Nitrophenol is not steam volatile due to presence of intermolecular H–bonding.

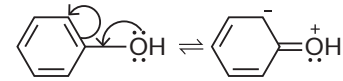


o-Nitrophenol



p-Nitrophenol

(ii) Due to resonance, C – O bond acquires some double bond character. So, in phenol, C – O bond length is smaller than methanol.



(iii) The reaction of dialkyl ether gives two alkyl halide molecules.

$$R—O—R + 2HX \rightarrow 2R—X + H_2O$$

Alkyl halide

CHAPTER

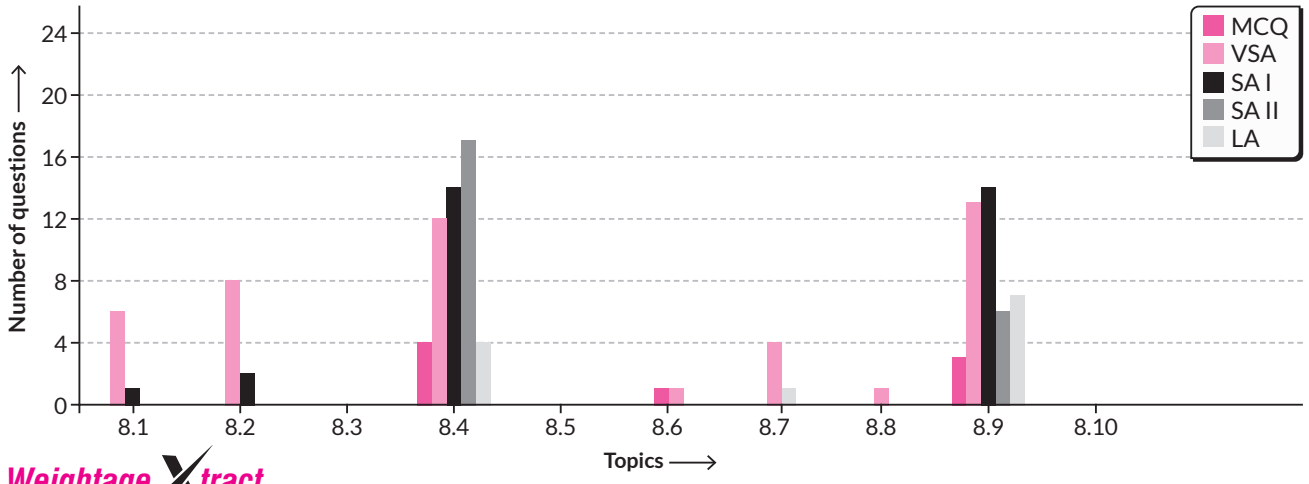
8

Aldehydes, Ketones and Carboxylic Acids

TOPICS

8.1 Nomenclature and Structure of Carbonyl Group
8.2 Preparation of Aldehydes and Ketones
8.3 Physical Properties
8.4 Chemical Reactions
8.5 Uses of Aldehydes and Ketones
8.6 Nomenclature and Structure of Carboxyl Group
8.7 Methods of Preparation of Carboxylic Acids
8.8 Physical Properties
8.9 Chemical Reactions
8.10 Uses of Carboxylic Acids

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topics 8.4 and 8.9 are highly scoring topics.
- Maximum total weightage is of Topic 8.4 *Chemical Reactions of Aldehydes and Ketones.*
- Maximum MCQ, VSA, SA I, SA II and LA type questions were asked from Topic 8.4 *Chemical Reactions of Aldehydes and Ketones.*

QUICK RECAP

ALDEHYDES AND KETONES

- **General formula :** $C_nH_{2n}O$ having $>C=O$ group.
  - **Aldehydes :** $\begin{matrix} R \\ H \end{matrix}\!\!>\!C=O$; where *R* = H, alkyl or aryl.
  - **Ketones :** $\begin{matrix} R \\ R \end{matrix}\!\!>\!C=O$; where *R* = alkyl or aryl.
- **Nomenclature :** The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –'*ic*' of acid with aldehyde.
  - The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –'*e*' with –'*al*' and –'*one*' respectively.
- **Structure:** The C-atom of carbonyl group is sp^2 hybridised and forms three σ-bonds and one π-bond with O atom. Carbonyl carbon with three atoms attached to it lie in a same plane with bond angle 120° (trigonal coplanar structure) and π-electron cloud lies above and below of this plane.
- **Preparation :**
  - **Oxidation of alcohols :**

$$RCH_2OH + [O] \xrightarrow[H_2SO_4\,(dil.)]{K_2Cr_2O_7} RCHO + H_2O$$

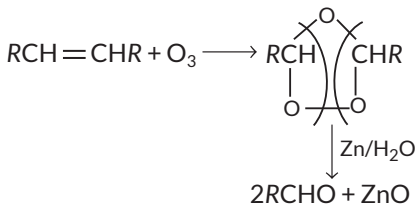
$$R_2CHOH + [O] \xrightarrow[H_2SO_4\,(dil.)]{K_2Cr_2O_7} R-\overset{\overset{O}{\|}}{C}-R + H_2O$$

- **Catalytic dehydrogenation of alcohols :**

$$RCH_2OH \xrightarrow[573\,K]{Cu} RCHO + H_2\uparrow$$

$$R_2CHOH \xrightarrow[573\,K]{Cu} R_2CO + H_2\uparrow$$

- **Reductive ozonolysis of alkenes :**



- **Rosenmund reduction :**

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{\text{Pd-BaSO}_4,\,S} RCHO + HCl$$

- **Reduction of nitriles :**

$$RC\equiv N \xrightarrow[(ii)\ H_2O]{(i)\ AlH(i\text{-}Bu)_2} RCHO$$

$$RC\equiv N \xrightarrow[(ii)\ H_3O^+]{(i)\ R'MgX/\text{dry ether}} RCOR'$$

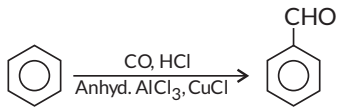
$$RC\equiv N \xrightarrow[\substack{\text{Dry ether}\\(ii)\ H_3O^+}]{(i)\ SnCl_2 + HCl} RCHO + NH_4Cl$$

(Stephen reduction)

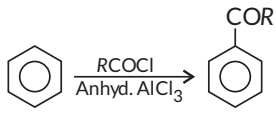
- **From esters :**

$$RCOOR \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL\text{-}H,\ 195\,K} RCHO$$

- **Gatterman–Koch reaction :**



- **Friedel–Crafts acylation :**

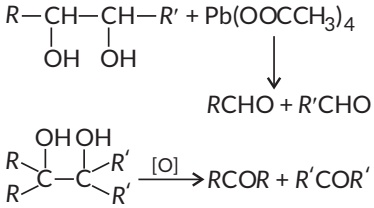


- **From alkynes :**

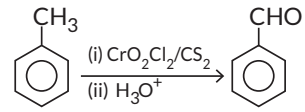
$$-C\equiv C- \xrightarrow[HgSO_4,\,333K]{dil.\ H_2SO_4} RCHO \text{ or } RCOR$$

$$-C\equiv C- \xrightarrow[H_2O_2/\,OH^-]{B_2H_6,\,THF} RCHO \text{ or } RCOR$$

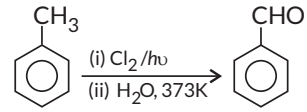
- **Oxidation of 1,2-glycols :**



- **Etard reaction :**



- **Side chain chlorination :**

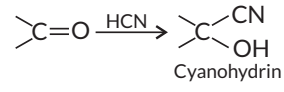


Physical properties :

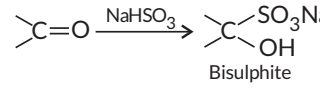
- **Physical state :** Lower members of aldehydes and ketones (upto C_{10}) are colourless, volatile liquids except formaldehyde which is gas at ordinary temperature.
  - Higher members of aldehydes and ketones are solids with fruity odour.
  - Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
- **Boiling points :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak dipole-dipole interactions.
  - Their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
  - Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.
- **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular weight.
  - Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
  - All carbonyl compounds are fairly soluble in organic solvents.

Chemical properties :

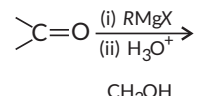
- **Nucleophilic addition reactions :**

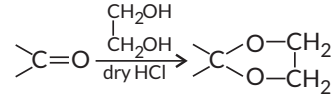


Cyanohydrin

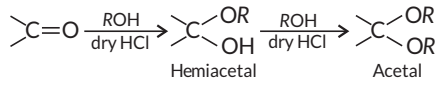


Bisulphite

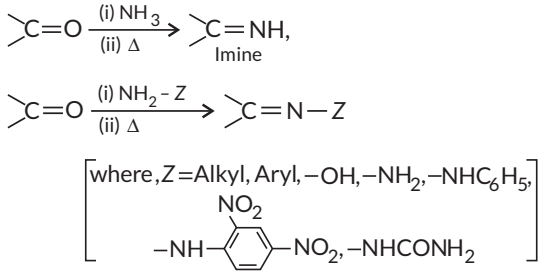




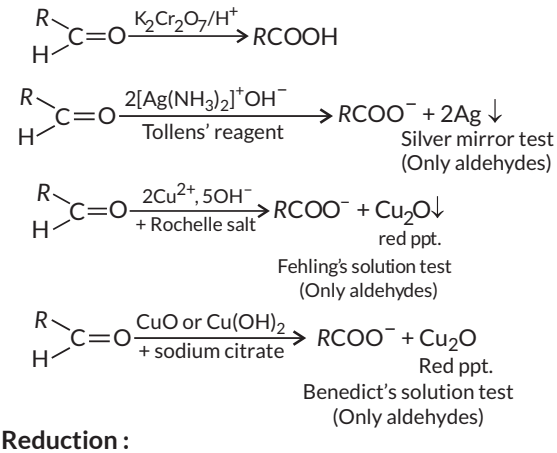
Ethylene glycol ketal



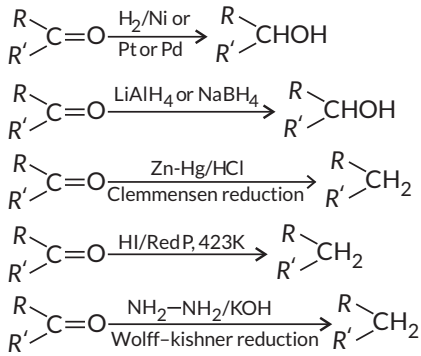
▶ **Nucleophilic addition-elimination reactions :**



▶ **Oxidation :**



▶ **Reduction :**



▶ **Haloform reaction :**

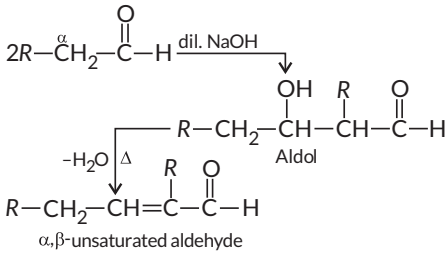
$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

$RCOCH_3 + 3NaOI \longrightarrow RCOONa + CHI_3\downarrow + 2NaOH$

Iodoform (yellow ppt.)

(Given by compounds having CH_3CO- group or $CH_3CH(OH)-$ group).

▶ **Aldol condensation :**

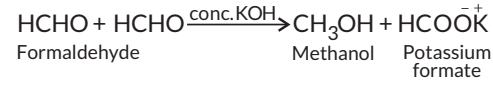


(Aldehydes and ketones having at least one α-hydrogen.)

– **Intramolecular aldol condensation :** It takes place in diketones and gives rise to cyclic products.

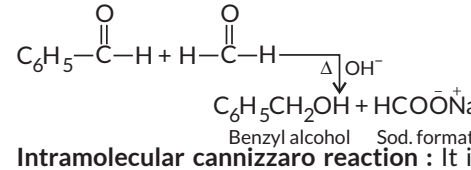
– **Crossed aldol condensation :** Aldol condensation is carried out between two different aldehydes and/or ketones and if both of them contain α-hydrogen atoms, it gives a mixture of four products.

▶ **Cannizzaro reaction :**



(Aldehydes which do not have an α-hydrogen atom.)

– **Crossed Cannizzaro reaction :**



– **Intramolecular cannizzaro reaction :** It is given by dialdehydes having no α-hydrogen atoms.

▶ **Electrophilic substitution reactions :** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.

Distinction between aldehydes and ketones :

Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-Dinitrophenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.

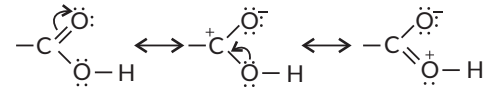
CARBOXYLIC ACIDS

General Formula : $C_nH_{2n}O_2$ having $-COOH$ group.
$RCOOH$ where, R = H or alkyl or aryl.

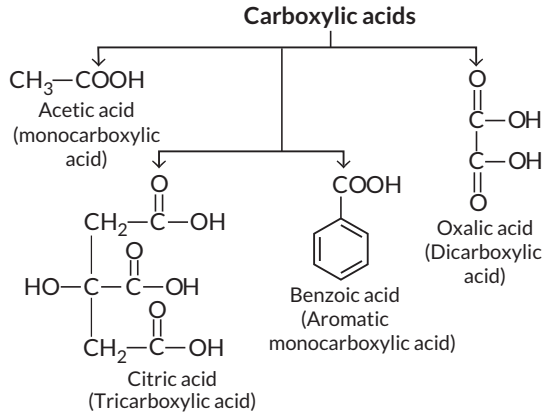
Nomenclature : The common names end with the suffix *–'ic acid'* and have been derived from Latin or Greek names of their natural sources.

▶ In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending *–'e'* in the name of the corresponding alkane with *–'oic acid'*. In numbering the carbon chain, the carboxylic carbon is numbered one.

Structure : In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



Classification : They are classified as mono, di, tri and polycarboxylic acids depending upon the number of carboxyl groups present in a molecule.



Aliphatic monocarboxylic acids and aliphatic esters are known as *functional isomers*. Some higher aliphatic monocarboxylic acids (C_{12}—C_{18}) are known as *fatty acids* because they occur in natural fats as esters of glycerol, *e.g.*, palmitic acid and stearic acid are obtained on hydrolysis of fats.

Preparation :

$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow[\text{or } K_2Cr_2O_7 + \text{dil. } H_2SO_4]{\text{Oxidation, alk. } KMnO_4,\ H_3O^+ \text{ or } CrO_3 - H_2SO_4 \text{ (Jones reagent)}} RCOOH$$

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[\text{or Fehling's solution or Tollens' reagent}]{\text{Oxidation } K_2Cr_2O_7 + \text{dil. } H_2SO_4} RCOOH$$

$$\underset{\text{cyanide}}{RCN} \xrightarrow[\text{Mineral acid HCl, } H_2SO_4, \text{ etc.}]{\text{Hydrolysis}} RCOOH$$

$$\underset{\text{cyanide}}{RCN} \xrightarrow[\text{Alkali NaOH or KOH}]{\text{Hydrolysis}} RCOONa \xrightarrow{HCl} RCOOH$$

$$\underset{\text{Grignard reagent}}{RMgX} \xrightarrow[\text{dry ether}/H_3O^+]{CO_2\text{(dry ice)}} RCOOH$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[\Delta]{H_3O^+} RCOOH$$

$$\underset{\text{Acyl halide}}{RCOCl} \xrightarrow[\text{or, (i) } OH^-/H_2O \text{ (ii) } H_3O^+]{H_2O} RCOOH$$

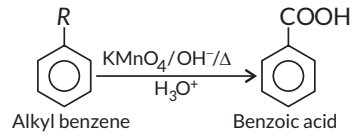
$$(RCO)_2O \xrightarrow{H_2O} \underset{\text{Acid anhydride}}{RCOOH}$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{H_3O^+,\ \Delta} RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{NaOH,\ H_3O^+} RCOOH$$

$$\underset{\text{Alkene}}{RCH=CHR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$

$$\underset{\text{Alkyne}}{RC\equiv CR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$



Physical Properties :

- **Physical state :** The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.
- **Odour :** The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.
- **Solubility :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
  - The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
  - Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.
  - Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.
- **Boiling points :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of their molecules through intermolecular hydrogen bonding. The H-bonds are not broken completely even in the vapour phase.

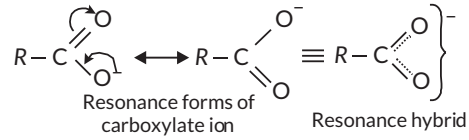
Acidity of Carboxylic Group :

- The acidic character of carboxylic acids is due to release of H^+ ion in aqueous solution.

  $RCOOH \rightleftharpoons RCOO^- + H^+$

  This is explained with the help of resonance.

  The resonating structures are as follows :



  Due to electronegativity of oxygen atom, it attracts the electrons of the O—H bond towards itself. This helps in release of hydrogen as proton.

  Thus, the acidity of carboxylic acid is due to powerful resonance stabilisation of the anion.

Chemical reactions :

- **Reactions involving cleavage of O—H bond :**

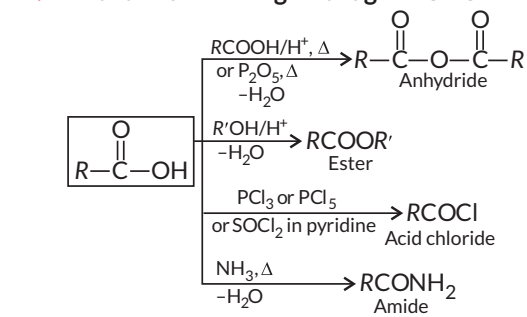
$$R-C(=O)-OH \xrightarrow{Na_2CO_3} RCOONa + CO_2 + H_2O$$

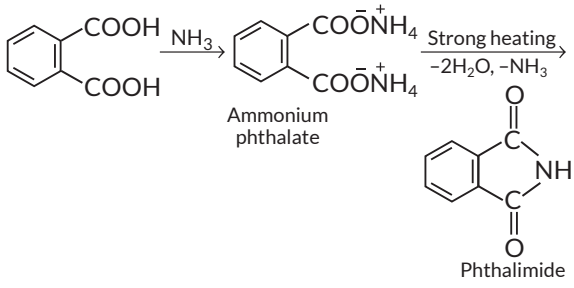
$$R-C(=O)-OH \xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$

$$R-C(=O)-OH \xrightarrow{Na} RCOONa + 1/2\ H_2$$

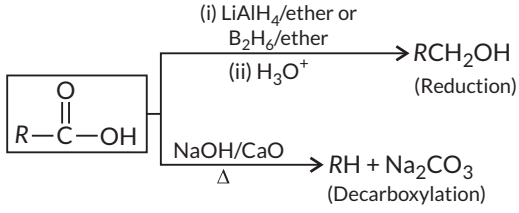
$$R-C(=O)-OH \xrightarrow{NaOH} RCOONa + H_2O$$

▶ **Reactions involving cleavage of C—OH bond :**

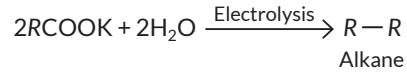




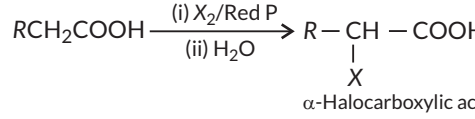
▶ **Reactions involving —COOH group :**



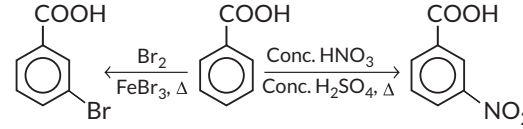
▶ **Kolbe's Electrolysis :** Sodium or Potassium salts of carboxylic acids on electrolysis give hydrocarbons containing double the number of carbon atoms present in the alkyl group of the acid.



▶ **Hell–Volhard–Zelinsky reaction :**



▶ **Ring substitution in aromatic acids :** Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a *deactivating* and *meta* directing group.



Distinction test between phenol and carboxylic acid:

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	No reaction	Brisk effervescence of CO_2 gas.
$FeCl_3$ test	Violet colour	Buff coloured ppt.

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Aldehydes

General formula : $C_nH_{2n+1}CHO$; **IUPAC name :** Alkanals

Physical Properties

- B.pt. of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak dipole-dipole interactions.
- B.pt. of aldehydes and ketones are lower than alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
- B.pt. of ketones are slightly higher than aldehydes due to the presence of two alkyl groups which make carbonyl group more polar.

B.pt. order:

Alcohols > Ketones > Aldehydes > Ethers > Hydrocarbons

- Solubility $\propto$ 1/Molecular mass
- Solubility in water is due to H-bonding between polar carbonyl group and water.
- Aromatic aldehydes and ketones are less soluble than corresponding aliphatic aldehydes and ketones due to large hydrocarbon part in benzene ring.

Haloform reaction:

Given by compounds having CH_3CO— group or $CH_3CH(OH)$— group

$$RCOCH_3 \xrightarrow{NaOX} \underset{\text{Haloform}}{RCOONa} + CHX_3 + NaOH$$

Aldol condensation:

- Aldehydes and ketones having at least one α-H atom undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively.
- The aldol and ketol readily lose water to give α, β-unsaturated carbonyl compounds.

Cannizzaro reaction:

Aldehydes which do not have α-H atom undergo disproportionation on heating with concentrated alkali.

Reaction involving —COOH group

$$R\text{—}COOH \xrightarrow[\Delta \text{ (Decarboxylation)}]{NaOH \text{ and } CaO} RH + Na_2CO_3$$

Reaction involving —*R* group

$$RCH_2\text{—}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red P}} \underset{\underset{X}{|}}{R\text{—}CH\text{—}COOH}$$

α-Halocarboxylic acid

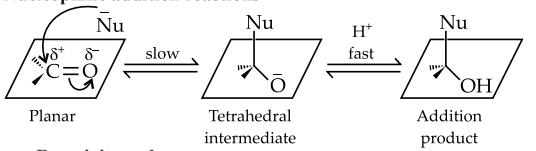
(Hell–Volhard–Zelinsky reaction)

Ketones

General formula : $C_nH_{2n+1}COC_nH_{2n+1}$; **IUPAC name :** Alkanones

Chemical Properties

Nucleophilic addition reactions



- **Reactivity order:**

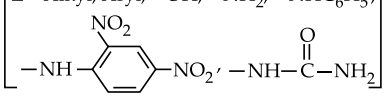
  Aldehydes > Ketones (steric and electronic reasons)

  HCHO > *R*CHO > PhCHO > *R*COR > *R*COPh > PhCOPh

Nucleophilic addition-elimination reactions

$$>C=O \xrightarrow[(ii)\ \Delta]{(i)\ NH_3} >C=NH + H_2O \quad \text{(Imine)}$$

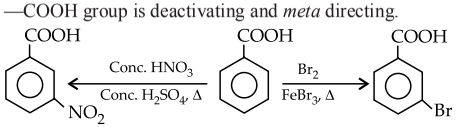
$$>C=O \xrightarrow[(ii)\ \Delta]{(i)\ NH_2\text{—}Z} >C=N\text{—}Z + H_2O$$

[Z = Alkyl, Aryl, —OH, —NH_2, —NHC_6H_5, ]

- $RCHO \xrightarrow{\text{Reduction}} RCH_2OH$
  $RCOR' \xrightarrow{\text{Reduction}} RCH(OH)R'$ (H_2/Ni or Pt or Pd, $LiAlH_4$ or $NaBH_4$)
- $RCHO \xrightarrow{\text{Reduction}} RCH_3$
  $RCOR' \xrightarrow{\text{Reduction}} RCH_2R'$ (Zn-Hg/HCl, NH_2NH_2/KOH, HI/Red P)
- $RCHO \xrightarrow{\text{Oxidation}} RCOOH$ (Even with mild oxidising agents) (same no. of C atoms)
- $RCOR' \xrightarrow{\text{Oxidation}} RCOOH$ (With strong oxidising agents) (lesser no. of C atoms)

Ring substitution in aromatic acids:

—COOH group is deactivating and *meta* directing.



Carboxylic Acids

General formula : $C_nH_{2n+1}COOH$; **IUPAC name :** Alkanoic acid

Physical Properties

- B.pt. of carboxylic acids are higher than aldehydes, ketones and alcohols of comparable molecular masses due to intermolecular H-bonding.

B.pt. order :

Carboxylic acids > Alcohols > Ketones > Aldehydes > Hydrocarbons

- In vapour phase or in aprotic solvents, they exist as dimer.
- Solubility $\propto$ 1/Number of C atoms
- Solubility in water is due to H-bonding.

Chemical Properties

- Carboxyl carbon is less electrophilic than carbonyl carbon.
- Hydroxyl group of acids is more acidic than the hydroxyl group of alcohols and phenols.
- Acidity order : Carboxylic acids > Phenols > Alcohols
- *EDG* decreases the acidity and *EWG* increases the acidity.
- More is the distance between the carboxyl group and electron withdrawing group, lesser will be the acidic strength.
- More is the electronegativity of the atom attached to the carboxyl group, more will be the acidity.

Reactions involving cleavage of —OH group

$$R\text{—}COOH \xrightarrow{+\ RCOOH/H^+,\Delta} (RCO)_2O \quad \text{Anhydride}$$

$$R\text{—}COOH \xrightarrow[-H_2O]{P_2O_5,\ \Delta} (RCO)_2O \quad \text{Anhydride}$$

$$R\text{—}COOH \xrightarrow[-H_2O]{R'OH/H^+} RCOOR' \quad \text{Ester}$$

$$R\text{—}COOH \xrightarrow{PCl_3 \text{ or } PCl_5 \text{ or } SOCl_2 \text{ in pyridine}} RCOCl \quad \text{Acid chloride}$$

$$R\text{—}COOH \xrightarrow[-H_2O]{NH_3,\ \Delta} RCONH_2 \quad \text{Amide}$$

Reactions involving proton of —OH group

$$R\text{—}COOH \xrightarrow{Na} 2RCOONa + H_2$$

$$R\text{—}COOH \xrightarrow{NaOH} RCOONa + H_2O$$

$$R\text{—}COOH \xrightarrow{Na_2CO_3} 2RCOONa + CO_2 + H_2O$$

$$R\text{—}COOH \xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$

Reaction involving $>C=O$ group

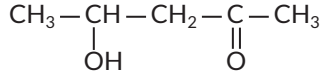
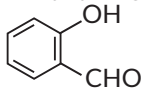
$$R\text{—}COOH \xrightarrow[(ii)\ H_3O^+ \text{ (Reduction)}]{(i)\ LiAlH_4/\text{ether or } B_2H_6/\text{ether}} RCH_2OH$$

BRAIN MAP

Previous Years' CBSE Board Questions

8.1 Nomenclature and Structure of Carbonyl Group

VSA (1 mark)

1. Write the structure of 2-methylbutanal. *(1/5, AI 2015)*
2. Draw the structure of 3-methylpentanal. *(Delhi 2015C)*
3. Write the IUPAC name of the following :
$CH_3—CH_2—CHO$ *(AI 2015C)*
4. Write the IUPAC name of the compound :

(Delhi 2014) Ap
5. Write the structure of 4-chloropentan-2-one. *(AI 2014)*
6. Write the IUPAC name of the following compound :

(Foreign 2014)

SA I (2 marks)

7. Draw the structures of the following :
(i) *p*-Methylbenzaldehyde
(ii) 4-Methylpent-3-en-2-one *(2/5, AI 2015C)*

8.2 Preparation of Aldehydes and Ketones

VSA (1 mark)

8. What happens when benzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$? *(1/2, 2020)* U
9. How can you convert the following : Benzene to acetophenone? *(1/3, 2020)*
10. Complete the following reaction :
$(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$ *(1/3, Delhi 2019)*
11. Write chemical equation for the following reaction:
Benzoyl chloride is hydrogenated in presence of $Pd/BaSO_4$. *(1/3, Delhi 2019, 1/5, 2018C)*
12. Write the equation involved in the following reaction:
Etard reaction. *(1/2, Delhi 2017)* R
13. Write the reaction involved in the following :
Stephen reduction. *(1/5, AI 2017)*
14. Write the product in the following reaction :
$CH_3—CH=CH—CN \xrightarrow[(b)\ H_2O]{(a)\ DIBAL-H}$? *(1/5, AI 2017)*

OR

Write the product in the following reaction :
$CH_3—CH=CH—CH_2CN \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL-H}$
(1/5, Delhi 2016)
15. How do you convert the following :
Ethyne to ethanal *(1/3, Foreign 2015)* An

SA I (2 marks)

16. Write the major product(s) in the following :
(i) $CH_3—CH=CH—CH_2—CN \xrightarrow[(ii)\ H_3O^+]{(i)\ DIBAL-H}$
(ii) $CH_3—CH_2—OH \xrightarrow{CrO_3}$ *(2/5, 2020)*
17. Write the equations involved in the following reactions :
(i) Stephen reaction
(ii) Etard reaction *(2/3, Foreign 2015)*

8.4 Chemical Reactions

MCQ

18. **Assertion :** The final product in Aldol condensation is always α, β-unsaturated carbonyl compound.
Reason : α, β-unsaturated carbonyl compounds are stabilised due to conjugation.
(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A)
(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A)
(c) Assertion (A) is true, but Reason (R) is False.
(d) Assertion (A) is false, but Reason (R) is true.
(2023)
19. Iodoform test is not given by
(a) ethanol (b) ethanal
(c) pentan-2-one (d) pentan-3-one
(2020) Ap
20. **Assertion (A) :** Reactivity of ketones is more than aldehydes.
Reason (R) : The carbonyl carbon of ketones is less electrophilic as compared to aldehydes.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*
21. **Assertion (A) :** Oxidation of ketones is easier than aldehydes.
Reason (R) : C-C bond of ketones is stronger than C-H bond of aldehydes.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is wrong statement.
(d) Assertion (A) is wrong, but Reason (R) is correct statement. *(2020)* An

VSA (1 mark)

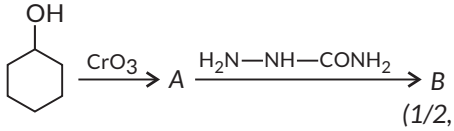
22. What happens when,
propanone is treated with methyl magnesium iodide and then hydrolysed? *(1/2, 2020)*

23. How can you convert the following : Acetone to propene ? *(1/3, 2020)* An

OR

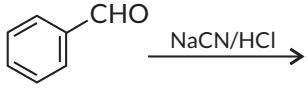
Do the following conversion in not more than two steps :
Propanone to propene *(1/3, Delhi 2017)*

24. Write structures of compounds *A* and *B* in the following reaction :



(1/2, Delhi 2019)

25. Complete the following reaction :



(1/3, Delhi 2019)

26. How do you convert the following :
Ethanal to propanone *(1/2, 2018)*

27. Give simple chemical tests to distinguish between the following pair of compounds :
Ethanal and propanal *(1/5, 2018C)*

28. Give chemical tests to distinguish between the following pair of compounds :
Benzaldehyde and acetophenone.
(1/5, AI 2017C, 1/5, Delhi 2015C)

OR

Distinguish between the following :
$C_6H_5—COCH_3$ and $C_6H_5—CHO$
(1/2, AI 2016, 1/5, AI 2015)

29. Write the structures of *A* and *B* in the following reaction :
$CH_3COCl \xrightarrow{H_2, Pd - BaSO_4} A \xrightarrow{H_2N—OH} B$ *(1/5, AI 2016)*

30. Give a simple chemical test to distinguish between the following pair of compounds :
CH_3CH_2CHO and $CH_3CH_2COCH_3$
(1/2, AI 2016, 1/5, AI 2015)

OR

Give simple chemical tests to distinguish between the following pair of compounds :
Propanal and butan-2-one *(1/5, Foreign 2014)*

31. Name the reagent used in the following reaction :

$$CH_3—CO—CH_3 \xrightarrow{?} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

(Delhi 2015, 1/2, Foreign 2015)

32. Give simple chemical tests to distinguish between the following pairs of compounds :
(i) Benzaldehyde and benzoic acid
(ii) Propanal and propanone. *(1/5, Delhi 2014)* An

OR

Give simple chemical tests to distinguish between the following pair of compounds :
Propanal and propanone *(1/5, AI 2014)*

33. Account for the following :
CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. *(Delhi 2014)*

SA I (2 marks)

34. Write the products formed when benzaldehyde reacts with the following reagents (Any two) :
(i) CH_3CHO in presence of dilute NaOH
(ii) $H_2N—OH$ in presence of weak acid
(iii) Tollens' reagent *(Term II, 2021-22)* R

35. Explain the following reactions:
(a) Wolff–Kishner reduction
(b) Cannizzaro reaction *(Term II, 2021-22)*

36. Write chemical equations for the following reactions:
(i) Propanone is treated with dilute $Ba(OH)_2$.
(ii) Acetophenone is treated with Zn(Hg)/Conc. HCl
(2/3, Delhi 2019)

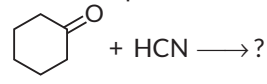
37. Write the structure of major product(s) in the following :

(i) $CH_3—CH_2—\underset{\displaystyle O}{\underset{\|}{C}}—H \xrightarrow[\text{(b) KOH, glycol/heat}]{\text{(a) } H_2N—NH_2}$

(ii) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}(CH_3)—CHO \xrightarrow{\text{conc. NaOH}}$

(2/5, AI 2019)

38. (a) Write the product in the following reaction :



(b) Give simple chemical test to distinguish between the following pair of compounds :
Butanal and Butan-2-one *(2/5, AI 2017)*

39. Write the equations involved in the following reactions :
(i) Clemmensen reduction
(ii) Cannizzaro reaction *(Delhi 2017)*

40. Predict the products of the following reactions :

(i) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}(=O) \xrightarrow[\text{(ii) KOH/Glycol, } \Delta]{\text{(i) } H_2N—NH_2} ?$

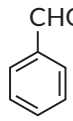
(ii) $C_6H_5—CO—CH_3 \xrightarrow{NaOH/I_2} ? + ?$ *(2/3, Delhi 2015)*

41. A compound '*A*' of molecular formula C_2H_3OCl undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C* and *D* in the following reactions :

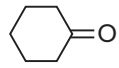
$(C_2H_3OCl)A \xrightarrow{H_2/Pd\text{-}BaSO_4} B \xrightarrow{\text{dil. NaOH}} C \xrightarrow{\text{Heat}} D$

(AI 2015) Ap

42. Describe the following reactions :
(i) Acetylation
(ii) Aldol condensation *(2/5, Delhi 2015C)*

43. Write the main product in the following equations :
(i) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} ?$
(ii)  $\xrightarrow[273\text{-}283K]{HNO_3/H_2SO_4} ?$ *(2/5, Delhi 2015C)*

44. Draw the structures of the following derivatives :
(i) Propanone oxime
(ii) Semicarbazone of the CH_3CHO *(2/5, AI 2015C)*

45. (i)  $+ H_2N-OH \xrightarrow{H^+}$
(ii) $2C_6H_5CHO + \text{conc. NaOH} \longrightarrow$ *(2/5, Delhi 2014)*

46. Account for the following :
(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.
(ii) There are two $-NH_2$ groups in semicarbazide ($H_2NNHCONH_2$).
However, only one is involved in the formation of semicarbazone. *(2/5, Foreign 2014)* Ev

47. Write the chemical equation to illustrate each of the following name reactions :
(i) Rosenmund reduction
(ii) Cannizzaro reaction *(2/5, Foreign 2014)*

SA II (3 marks)

48. An organic compound '*A*' having the molecular formula C_3H_8O on treatment with Cu at 573 K, gives '*B*'. '*B*' does not reduce Fehling's solution but gives a yellow precipitate of the compound '*C*' with I_2/NaOH. Deduce the structures of *A*, *B* and *C*. *(2023)*

49. Write the equation involved in the following reactions :
(i) Rosenmund reduction
(ii) Etard reaction
(iii) Stephen reaction *(Term-II, 2021-22)*

50. (i) Which will undergo faster nucleophilic addition reaction – Acetaldehyde or propanone?
(ii) What is the composition of Fehling's reagent ?
(iii) Draw structure of the semicarbazone of ethanal
(Term II, 2021-22) R

51. What happens when
(i) Propanone is treated with CH_3MgBr and then hydrolysed ?
(ii) Ethanal is treated with excess ethanol and acid?
(iii) Methanal undergoes Cannizzaro reaction ?
(Term II, 2021-22) Ev

52. An organic compound '*X*' with the molecular formula $C_5H_{10}O$ forms 2,4-DNP derivative, does not reduce Tollens' reagent but gives positive iodoform test on heating with I_2 in the presence of NaOH. Compound '*X*' gives ethanoic acid and propanoic acid on vigorous oxidation. Write the
(i) Structure of the compound '*X*'.
(ii) Structure of the product obtained when compound '*X*' reacts with 2,4-DNP reagent.
(iii) Structures of the products obtained when compound '*X*' is heated with I_2 in the presence of NaOH. *(Term II, 2021-22)* Ap

53. Write the products formed when $(CH_3)_3C-CHO$ reacts with the following reagents :
(i) CH_3COCH_3 in the presence of dilute NaOH
(ii) HCN
(iii) Conc. NaOH *(2020)*

54. (a) How can you distinguish between propanal and propanone?
(b) Draw structures of the following derivatives :
(i) Cyanohydrin of cyclobutanone
(ii) Hemiacetal of ethanal *(3/5, 2020)*

55. An alkene *A* with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds, *B* and *C*. Compound *B* gives positive Fehling's test and also reacts with iodine and NaOH solution. Compound *C* does not give Fehling solution test but forms iodoform. Identify the compounds *A*, *B* and *C*.
(3/5, AI 2019) Ap

56. (*A*), (*B*) and (*C*) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (*A*) and (*C*) give positive Tollens' test whereas isomer (*B*) does not give Tollens' test but gives positive iodoform test. Isomers (*A*) and (*B*) on reduction with Zn(Hg)/conc. HCl give the same product (*D*).
(a) Write the structures of (*A*), (*B*), (*C*) and (*D*).
(b) Out of (*A*), (*B*) and (*C*) isomers, which one is least reactive towards addition of HCN?
(2018) Ev

57. (a) Write the chemical equation for the reaction involved in Cannizzaro reaction.
(b) Draw the structure of the semicarbazone of ethanal.
(c) How can you distinguish between propanal and propanone? *(3/5, Delhi 2016)*

58. (a) Write the chemical reaction involved in Wolff-Kishner reduction.
(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.
$C_6H_5COCH_3$, CH_3CHO, CH_3COCH_3
(c) *A* and *B* are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer *B* forms yellow precipitate of iodoform whereas isomer *A* does not form any precipitate. Write the formulae of *A* and *B*. *(3/5, AI 2016)*

59. Write the structures of the main products when acetone ($CH_3-CO-CH_3$) reacts with the following reagents :
(i) Zn—Hg/conc. HCl
(ii) $H_2N-NHCONH_2/H^+$
(iii) CH_3MgBr and then H_3O^+ *(3/5, AI 2015)*

60. How will you convert ethanal into the following compounds? Give the chemical equations involved.

(i) $CH_3—CH_3$

(ii) $CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—CHO$

(iii) CH_3CH_2OH *(3/5, Delhi 2015C)*

61. Write the chemical equations to illustrate the following name reactions :
(i) Wolff–Kishner reduction
(ii) Aldol condensation
(iii) Cannizzaro reaction *(3/5, Delhi 2014)*

62. Write the products formed when CH_3CHO reacts with the following reagents :
(i) HCN (ii) $H_2N—OH$
(iii) CH_3CHO in the presence of dilute NaOH
(3/5, AI 2014)

63. (a) Write the chemical equations to illustrate the following name reactions :
(i) Rosenmund reduction
(ii) Cannizzaro reaction
(b) Out of $CH_3CH_2—CO—CH_2—CH_3$ and $CH_3CH_2—CH_2—CO—CH_3$, which gives iodoform test? *(3/5, AI 2014)*

64. Write the products formed when ethanal reacts with the following reagents :
(i) CH_3MgBr and then H_3O^+
(ii) Zn-Hg/conc. HCl
(iii) C_6H_5CHO in the presence of dilute NaOH
(3/5, Foreign 2014) Ap

LA (5 marks)

65. (i) Carry out the following conversions :
(1) Ethanal to But-2-en-1-al
(2) Propanoic acid to 2-chloropropanoic acid
(ii) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds '*B*' and '*C*'. Compound '*B*' gives positive Fehling test and also reacts with iodine and NaOH solution. Compound '*C*' does not give Fehling solution test but forms iodoform. Identify the compounds '*A*', '*B*' and '*C*'. *(2023)*

66. (i) Write the reaction involved in Cannizzaro's reaction.
(ii) Why are the boiling point of aldehydes and ketones lower than that of corresponding carboxylic acids?
(iii) An organic compound '*A*' with molecular formula $C_5H_8O_2$ is reduced to *n*-pentane with hydrazine followed by heating with NaOH and glycol. '*A*' forms a dioxime with hydroxylamine and gives a positive iodoform and Tollen's test. Identify '*A*' and give its reaction for Iodoform and Tollen's test. *(2023)*

67. A compound '*A*' (C_2H_4O) on oxidation gives '*B*' ($C_2H_4O_2$). '*A*' undergoes iodoform reaction to give yellow precipitate and reacts with HCN to form the compound '*C*'. '*C*' on hydrolysis gives 2-hydroxypropanoic acid. Identify the compounds '*A*', '*B*' and '*C*'. Write down equations for the reactions involved.
(Term II, 2021-22) An

68. (a) An organic compound (*A*) having molecular formula C_4H_8O gives orange red precipitate with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow precipitate of iodoform on heating with NaOH and I_2. Compound (*A*) on reduction with $NaBH_4$ gives compound (*B*) which undergoes dehydration reaction on heating with conc. H_2SO_4 to form compound (*C*). Compound (*C*) on ozonolysis gives two molecules of ethanal. Identify (*A*), (*B*) and (*C*) and write their structures. Write the reactions of compound (*A*) with (i) $NaOH/I_2$ and (ii) $NaBH_4$.
(b) Give reason :
(i) Oxidation of propanal is easier than propanone.
(ii) α-Hydrogen of aldehydes and ketones is acidic in nature. *(2020)* An

8.6 Nomenclature and Structure of Carboxyl Group

MCQ

69. What is the correct IUPAC name of the given compound?

$$CH_3—\underset{\displaystyle COOH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}—CH_2—CH_3$$

(a) 2,2-Dimethylbutanoic acid
(b) 2-Carboxyl-2-methylbutane
(c) 2-Ethyl-2-methylpropanoic acid
(d) 3-Methylbutanecarboxylic acid *(2020)*

VSA (1 mark)

70. Write the IUPAC name of the compound :

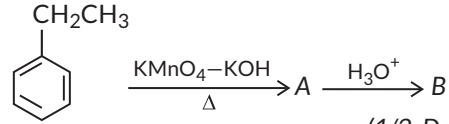
$$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—COOH$$

(Delhi 2014)

8.7 Methods of Preparation of Carboxylic Acids

VSA (1 mark)

71. Write structures of compounds *A* and *B* in each of the following reaction.



(1/2, Delhi 2019) An

72. How do you convert the following :
Toluene to benzoic acid? *(1/2, 2018)*

73. Do the following conversion in not more than two steps :
Ethyl benzene to benzoic acid *(1/3, Delhi 2017)*

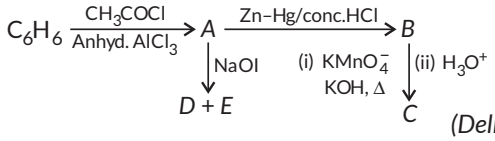
74. Name the reagent used in the following reaction :

$$C_6H_5—CH_2—CH_3 \xrightarrow{?} C_6H_5—COO^-K^+$$

(1/2, Delhi 2015)

LA (5 marks)

75. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions :



(Delhi 2016)

8.8 Physical Properties

VSA (1 mark)

76. Arrange the following in the increasing order of their boiling points.
CH_3CHO, CH_3COOH, CH_3CH_2OH
(1/5, AI 2016, 2015)

8.9 Chemical Reactions

MCQ

77. Which one of the following has lowest pK_a value?
(a) CH_3-COOH
(b) O_2N-CH_2-COOH
(c) $Cl-CH_2-COOH$
(d) HCOOH *(2023)*

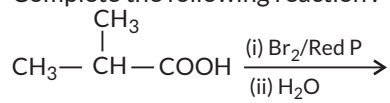
78. **Assertion :** Benzoic acid does not give Friedel-Crafts reaction.
Reason : The carboxyl group is deactivating and gets bonded to Lewis acid $AlCl_3$.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2021 C)* U

79. **Assertion (A) :** Benzoic acid does not undergo Friedal-Crafts reaction.
Reason (R) : The carboxyl group is activating and undergoes electrophilic substitution reaction.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

VSA (1 mark)

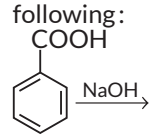
80. Arrange the following in the increasing order of the property mentioned :
(a) CH_3COOH, $ClCH_2COOH$, FCH_2COOH
(Acid strength)
(b) CH_3CHO, CH_3CH_2OH, $CH_3CH_2CH_3$
(Boiling points) *(Term II, 2021-22)*

81. Complete the following reaction :



(1/3, Delhi 2019)

82. Write the structure of major product(s) in the following :



(1/5, AI 2019)

83. Carry out the following conversions :
Propanoic acid to acetic acid. *(1/5, AI 2019)*

84. Do the following conversion in not more than two steps :
Benzoic acid to benzaldehyde.
(1/3, Delhi 2017, 1/5 Delhi 2015C)

85. Why carboxylic acid does not give reactions of carbonyl group? *(1/5, AI 2017C, 1/5, AI 2016)* An

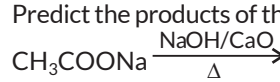
OR

Account for the following :
Carboxylic acids do not give reactions of carbonyl group. *(1/5, AI 2014)*

86. Give simple chemical tests to distinguish between the following pairs of compounds :
Benzoic acid and ethyl benzoate
(1/5, AI 2017C, 1/3, Foreign 2014)

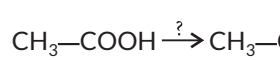
87. Distinguish between
CH_3COOH and HCOOH *(1/2, AI 2016)*

88. Predict the products of the following reaction :



(1/3, Delhi 2015)

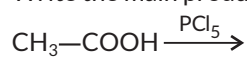
89. Name the reagent used in the following reaction :



(1/2, Foreign 2015) R

OR

Write the main product in the following equation :



(1/5, Delhi 2015C)

90. Describe the following giving chemical equation :
Decarboxylation reaction *(1/5, Delhi 2015C)*

91. Give simple chemical test to distinguish between the following pair of compounds :
Benzoic acid and phenol *(1/5, AI 2014)*

92. Write the chemical equation to illustrate the following name reaction :
Hell–Volhard–Zelinsky reaction
(1/5, Foreign 2014)

SA I (2 marks)

93. How will you carry out the following conversions : (Any two)
(i) Propanal to Propane
(ii) Ethanal to but-2-enal
(iii) Ethanoic acid to ethanamide *(Term II, 2021-22)*

94. Predict the reagent for carrying out the following transformations: (Any two)
(i) Benzoyl chloride to benzaldehyde
(ii) Ethanal to 3-hydroxy butanal
(iii) Ethanoic acid to 2-chloroethanoic acid
(Term II, 2021-22)

95. Arrange the following compounds in the increasing order of their property indicated : (Any two)
(i) Acetaldehyde, Benzaldehyde, Acetophenone, Acetone (Reactivity towards HCN)
(ii) $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ (Acidic strength)
(iii) CH_3CH_2OH, CH_3CHO, CH_3COOH (Boiling point)
(Term II, 2021-22) Ap

96. Write reasons for the following statements :
(i) Benzoic acid does not undergo Friedel-Crafts reaction.
(ii) Oxidation of aldehydes is easier than that of ketones. *(Term II, 2021-22)* Ev

97. Give reasons for the following statements : (Any two)
(i) Benzaldehyde is less reactive than propanal in nucleophilic addition reactions.
(ii) Carboxylic acids do not give reactions of carbonyl group.
(iii) 4-Nitrobenzoic acid is a stronger acid than benzoic acid. *(Term II, 2021-22)*

98. (i) Which acid of the following pair would you expect to be stronger ?
$F—CH_2—COOH$ or $CH_3—COOH$
(ii) Arrange the following compounds in increasing order of their boiling points :
CH_3CH_2OH, $CH_3—CHO$, $CH_3—COOH$
(iii) Give simple chemical test to distinguish between benzaldehyde and acetophenone.
(Term II, 2021-22)

99. (a) Arrange the following compounds in the increasing order of their acidic strength :

$F—CH_2—COOH, NO_2—CH_2—COOH, C_6H_5—COOH$

(b) Write the IUPAC name of the given compound :

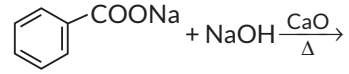
$CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—H$ *(Term II, 2021-22C)*

100. Arrange the following in the increasing order of their property indicated :
(a) Ethanal, Propanone, Propanal, Butanone (reactivity towards nucleophilic addition)
(b) 4-Nitrobenzoic acid, benzoic acid, 3, 4-Dinitrobenzoic acid
4-Methoxy benzoic acid (Acid strength)
(Term II, 2021-22)

101. Account for the following :
(a) Aromatic carboxylic acids do not undergo Friedel–Crafts reaction.
(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. *(2018)*

102. Write the reactions involved in the following :
(i) Hell—Volhard—Zelinsky reaction
(ii) Decarboxylation reaction *(Delhi 2017)*

103. (a) Write the product in the following reaction :



(b) Give simple chemical test to distinguish between the following pair of compounds :
Benzoic acid and phenol *(2/5, AI 2017)*

104. How will you convert the following in not more than two steps :
(i) Acetophenone to benzoic acid
(ii) Ethanoic acid to 2-hydroxyethanoic acid
(2/5, AI 2017)

105. (a) Write the product of the following reaction :

$CH_3COOH \xrightarrow{Cl_2/P}$

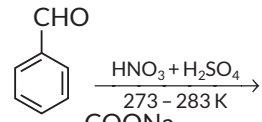
(b) Give simple chemical test to distinguish between the following pair of compounds :
Benzaldehyde and benzoic acid *(2/5, Delhi 2014)*

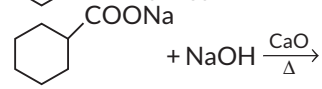
106. Account for the following :
$Cl—CH_2COOH$ is a stronger acid than CH_3COOH.
(2/5, AI 2014)

SA II (3 marks)

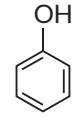
107. Explain why :
(i) Carboxyl group in benzoic acid is *meta* directing.
(ii) Sodium bisulphite is used for the purification of aldehydes and ketones.
(iii) Carboxylic acids do not give characteristic reactions of carbonyl group. *(2023)*

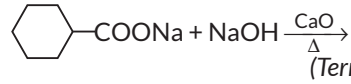
108. Write the major products in the following :

(i) 

(ii) 

(iii) $CH_3—\overset{\overset{H}{|}}{C}=O \xrightarrow{NH_2OH}$ *(Term II, 2021-22)*

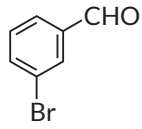
109. (i) Which acid of each pair would you expect to be stronger ? Give reason.
(I) CH_3COOH or $F—CH_2—COOH$
(II)  or $CH_3—COOH$
(ii) Distinguish between Pentan-2-one and Pentan-3-one. *(Term II, 2021-22)*

110. Write the main product in the following reactions:
(i) $2CH_3COCl + (CH_3)_2Cd \rightarrow$
(ii) $CH_3CH_2CHO \xrightarrow{Zn(Hg)/Conc.\ HCl}$
(iii) 
(Term II, 2021-22) Ap

111. (a) Complete the following :

(i) $CH_3CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} \text{'}A\text{'} \xrightarrow[H^+]{H_2N\text{-}OH} \text{'}B\text{'}$

(ii) Write IUPAC name of the following compound :



(iii) Write chemical test to distinguish between the following compounds : Phenol and Benzoic acid

OR

(b) Convert the following :

(i) Benzoic acid to benzaldehyde

(ii) Propan-1-ol to 2-bromopropanoic acid

(iii) Acetaldehyde to but-2-enal

(Term II, 2021-22) Ap

112. Write the structures of compounds *A*, *B* and *C* in each of the following reactions :

(i) $C_6H_5Br \xrightarrow{Mg/dry\ ether} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_{2(g)}} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{dil.\ NaOH} B \xrightarrow{\Delta} C$

(Delhi 2017)

LA (5 marks)

113. (i) Distinguish with a suitable chemical test :

(1) $CH_3COCH_2CH_3$ and $CH_3CH_2CH_2CHO$

(2) Ethanal and Ethanoic acid

(ii) Write the structure of oxime of acetone.

(iii) Identify *A* to *D*.

$$CH_3COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd\text{-}BaSO_4} B \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} C$$

$$B \xrightarrow{LiAlH_4} D$$

(2023)

114. (i) Give a chemical test to distinguish between ethanal and ethanoic acid.

(ii) Why is the α-hydrogen of aldehydes and ketones acidic in nature?

(iii) An organic compound '*A*' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds '*B*' and '*C*'. Oxidation of *C* with acidified potassium permanganate also produces '*B*'. Sodium salt of '*B*' on heating with soda lime gives methane.

(1) Identify '*A*', '*B*' and '*C*'.

(2) Out of '*B*' and '*C*', which will have higher boiling point? Give reason. *(2023)*

115. Read the passage given below and answer the questions that follow :

Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules due to higher electronegativity of oxygen relative to carbon in the carbonyl group. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled reduction of acyl halides. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes.

Aldehydes and ketones undergo nucleophilic addition reaction onto the carbonyl group but carboxylic acid does not undergo nucleophilic addition reaction. The alpha (α) -hydrogens of aldehydes and ketones are acidic. Therefore aldehydes and ketones having at least one α-hydrogen undergo Aldol condensation.

Aldehydes are easily oxidised by mild oxidising agents such as Tollens' reagent and Fehling's reagent. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and by hydrolysis of nitriles. Aromatic carboxylic acids are prepared by side-chain oxidation of alkyl benzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

(a) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction. :

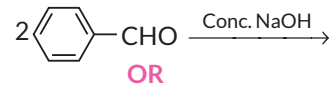
CH_3COCH_3, CH_3CHO, HCHO, $C_6H_5COCH_3$

(b) Give a simple chemical test to distinguish between Ethanal and Propanone.

(c) Why carboxylic acid does not give nucleophilic addition reactions like aldehydes and ketones?

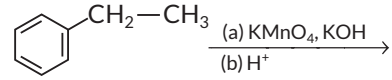
(d) (i) Why α-hydrogen of aldehydes and ketones are acidic in nature?

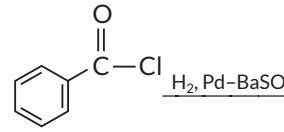
(ii) Write the products in the following:



OR

Write the major products of the following reactions:

(i) 

(ii) 

(Term II, 2021-22)

116. Read the following passage and answer the questions that follow :

A class of organic molecules which contain a carbon atom connected to an oxygen atom by a double bond are called Aldehydes and Ketones. It is called as carbonyl group. Aldehydes are prepared by the oxidation of alcohols. Formaldehyde is sold in an aqueous solution called formalin. Propanone, a simplest ketone is commercially prepared by fermenting corn or by oxidation of propan-2-ol. Carboxylic acids also have carbonyl carbon. They can be prepared by the oxidation of alcohols and aldehydes.

Formic acid was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings. Aldehydes undergo many nucleophilic addition reactions. They can be reduced to primary alcohols. The aldehydes with α-hydrogen undergo aldol condensation and the

aldehydes without α-hydrogen undergo Cannizzaro reaction.

Ketones are highly reactive, although less so than aldehydes. Ketones are obtained by oxidation of secondary alcohols. Ketones possessing α-hydrogens also undergo aldol condensation. Carboxylic acids occur widely in nature and are used in the production of plastics, esters, etc. Aspirin is prepared from acetic acid. Similar to aldehydes and ketones, carboxylic acids can be halogenated at the α-carbon by reacting with a halogen in presence of phosphorus.

(a) Which of the following compounds would undergo aldol condensation?
Methanal, Benzaldehyde, Ethanal

(b) Write the chemical test to distinguish between propanal and propanone.

(c) Write the reagent required in the following reaction:

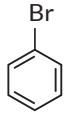
$CH_2{=}CH{-}CH_2OH \xrightarrow{?} CH_2{=}CH{-}CHO$

(d) (i) An alcohol '*A*', (C_3H_8O) on oxidation gives compound '*B*'. '*B*' gives negative Tollens' test and reacts with hydrazine to give compound '*C*'. '*B*' reacts with NaOH and I_2 to give yellow precipitate of '*D*'. Identify '*A*', '*B*', '*C*' and '*D*'.

OR

(ii) Write the chemical reactions for the following:
(I) Clemmensen reduction
(II) HVZ reaction *(Term II, 2021-22C)*

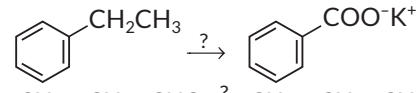
117. (i) Identify *A*, *B* and *C* in the following reactions:

(I)  $\xrightarrow{Mg,\ dry\ ether} A \xrightarrow[(ii)\ H_2O]{(i)\ CO_2} B \xrightarrow{PCl_5} C$

(II) $CH_3{-}CH_2OH \xrightarrow{CrO_3} A \xrightarrow{dil.\ NaOH} B \xrightarrow{\Delta} C$

(ii) By what tests will you distinguish between:
(I) Ethanol and Benzaldehyde
(II) Acetone and Acetic acid *(2021C)*

118. (i) Name the reagents used in the following reactions:

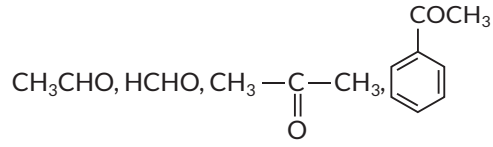
(I) 

(II) $CH_2{=}CH{-}CHO \xrightarrow{?} CH_2{=}CH{-}CH_2{-}OH$

(ii) Write the structure of oxime of propanal.

(iii) Why does carboxylic acid not give reactions of aldehydes and ketones?

(iv) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction:



(2021C)

119. (a) Write the products formed when benzaldehyde reacts with the following reagents :
(i) CH_3CHO in presence of dilute NaOH
(ii) H_2N-NH-
(iii) Conc. NaOH

(b) Distinguish between following :
(i) $CH_3-CH=CH-CO-CH_3$ and $CH_3-CH_2-CO-CH=CH_2$
(ii) Benzaldehyde and Benzoic acid. *(2020)* An

CBSE Sample Questions

8.2 Preparation of Aldehydes and Ketones

MCQ

1. The oxidation of toluene to benzaldehyde by chromyl chloride is called
(a) Etard reaction
(b) Riemer-Tiemann reaction
(c) Stephen's reaction
(d) Cannizzaro's reaction. *(2022-23)*

8.4 Chemical Reactions

MCQ

2. Which of the following tests/ reactions is given by aldehydes as well as ketones?
(a) Fehling's test (b) Tollens' test
(c) 2,4-DNP test (d) Cannizzaro reaction
(2022-23)

SA I (2 marks)

3. Write the reaction and IUPAC name of the product formed when 2-methylpropanal (*iso*-butyraldehyde) is treated with ethyl magnesium bromide followed by hydrolysis. *(2022-23)*

4. Give reasons to support the answer :
(a) Presence of alpha hydrogen in aldehydes and ketones is essential for aldol condensation.
(b) 3-Hydroxypentan-2-one shows positive Tollens' test. *(Term II, 2021-22)*

SA II (3 marks)

5. An alkene '*A*' (Mol. formula C_5H_{10}) on ozonolysis gives a mixture of two compounds '*B*' and '*C*'. Compound '*B*' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound '*C*' does not give Fehling's test but forms iodoform. Identify the compounds *A*, *B* and *C*. Write the reactions for ozonolysis and formation of iodoform from *B* and *C*.
(Term II, 2021-22)

LA (5 marks)

6. A hydrocarbon (*A*) with molecular formula C_5H_{10} on ozonolysis gives two products (*B*) and (*C*). Both (*B*) and (*C*) give a yellow precipitate when heated with iodine in presence of NaOH while only (*B*) gives a silver mirror on reaction with Tollen's reagent.
   (a) Identify (*A*), (*B*) and (*C*).
   (b) Write the reaction of *B* with Tollen's reagent.
   (c) Write the equation for iodoform test for *C*.
   (d) Write down the equation for aldol condensation reaction of *B* and *C*.

   OR

   An organic compound (*A*) with molecular formula $C_2Cl_3O_2H$ is obtained when (*B*) reacts with red P and Cl_2. The organic compound (*B*) can be obtained on the reaction of methyl magnesium chloride with dry ice followed by acid hydrolysis.
   (a) Identify *A* and *B*.
   (b) Write down the reaction for the formation of *A* from *B*. What is this reaction called?
   (c) Give any one method by which organic compound *B* can be prepared from its corresponding acid chloride.
   (d) Which will be the more acidic compound (*A*) or (*B*)? Why?
   (e) Write down the reaction to prepare methane from the compound (*B*). *(2022-23)*

7. An organic compound '*A*' C_8H_6 on treatment with dilute H_2SO_4 containing mercuric sulphate gives compound '*B*'. This compound '*B*' can also be obtained from a reaction of benzene with acetyl chloride in presence of anhy. $AlCl_3$. '*B*' on treatment with I_2 in *aq*. KOH gives '*C*' and a yellow compound '*D*'. Identify '*A*', '*B*', '*C*' and '*D*'. Give the chemical reactions involved.

   OR

   (i) Write the reaction for cross aldol condensation of acetone and ethanal.
   (ii) How will you carry out the following conversions:
   (a) Benzyl alcohol to phenyl ethanoic acid
   (b) Propanone to propene
   (c) Benzene to *m*-nitroacetophenone *(2020-21)*

8.9 Chemical Reactions

MCQ

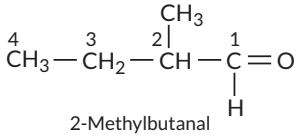
8. **Assertion :** Carboxylic acids are more acidic than phenols.
   Reason : Phenols are *ortho* and *para*-directing.
   (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
   (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
   (c) Assertion is correct statement but reason is wrong statement.
   (d) Assertion is wrong statement but reason is correct statement. *(2020-21)*

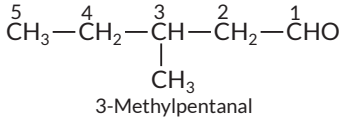
SA I (2 marks)

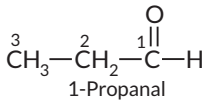
9. Arrange the following in the increasing order of their property indicated (any 2):
   (a) Benzoic acid, Phenol, Picric acid, Salicylic acid (pK_a values).
   (b) Acetaldehyde, Acetone, Methyl *tert*-butyl ketone (reactivity towards NH_2OH).
   (c) Ethanol, Ethanoic acid, Benzoic acid (boiling point) *(Term II, 2021-22)*

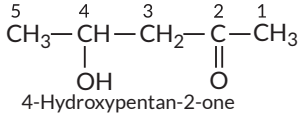
Detailed SOLUTIONS

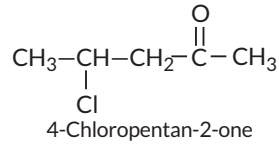
Previous Years' CBSE Board Questions

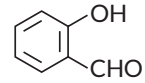
1. 
2-Methylbutanal

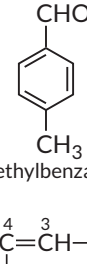
2. 
3-Methylpentanal

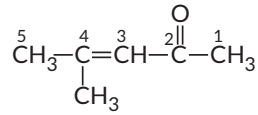
3. 
1-Propanal

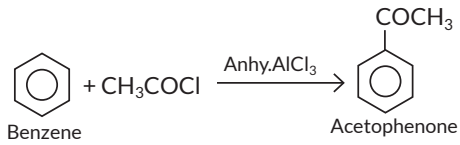
4. 
4-Hydroxypentan-2-one

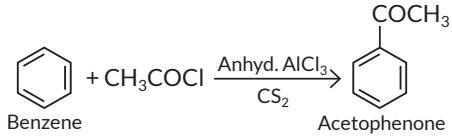
5. 
4-Chloropentan-2-one

6. 
2-Hydroxybenzaldehyde

7. (i) 
p-Methylbenzaldehyde

(ii) 
4-Methylpent-3-en-2-one

8. 

9. 

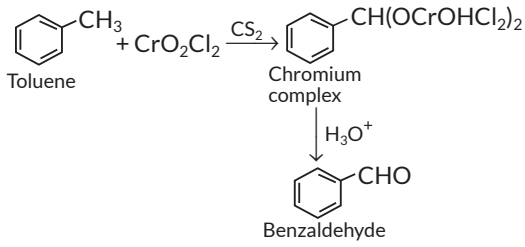
Answer Tips

➲ Use Friedel Crafts acylation reaction.

10. $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-CH_2C_6H_5 + CdCl_2$

11. $C_6H_5COCl \xrightarrow[Pd\text{-}BaSO_4]{H_2} C_6H_5CHO$
Benzoyl chloride — Benzaldehyde

12. **Etard reaction :**



13. **Stephen reduction :**

$R-CN + SnCl_2 + HCl \xrightarrow{\text{Dry ether}} R-CH=NH \xrightarrow{H_3O^+} R-CHO$

14. $CH_3-CH=CH-CN \xrightarrow{\text{(a) DIBAL-H}} CH_3-CH=CH-CH=NH \xrightarrow{\text{(b) } H_2O} CH_3-CH=CH-CHO$

OR

$CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3-CH=CH-CH_2CHO$

Important Part

➲ DIBAL-H (diisobutyl aluminium hydride) converts —CN group to —CHO in presence of H_2O. While conjugated double bond remains unaffected.

15. $CH\equiv CH \xrightarrow[HgSO_4]{dil.\ H_2SO_4} CH_3-CHO$
Ethyne — Ethanal

16. (i) $CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3-CH=CH-CH_2CHO$

(ii) $CH_3-\overset{OH}{\overset{|}{C}}H-H \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-H$

Commonly Made Mistake

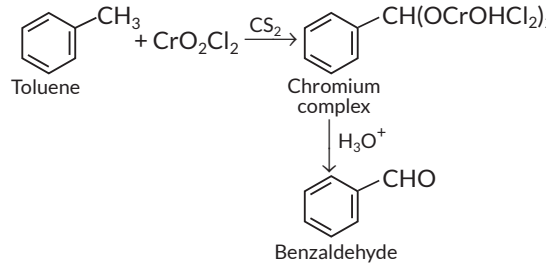
➲ CrO_3 is a mild oxidising agent, it oxidises alcohol to aldehyde and not to acid.

$R-CH_2OH \xrightarrow{CrO_3} R-\overset{O}{\overset{\|}{C}}-H$

17. (i) **Stephen reduction :**

$R-CN + SnCl_2 + HCl \xrightarrow{\text{Dry ether}} R-CH=NH \xrightarrow{H_3O^+} R-CHO$

(ii) **Etard reaction :**



18. (a): Aldehydes and ketones having at least one α-hydrogen atom undergo self condensation in the presence of dilute alkali to form β-hydroxyaldehydes (aldol) and β-hydroxyketones (ketol). This reaction is called aldol condensation.

The aldols and ketols readily lose water molecule to give α, β– unsaturated carbonyl compounds.

e.g., $2CH_3-CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO$
Ethanal — 3-Hydroxybutanal (Aldol)

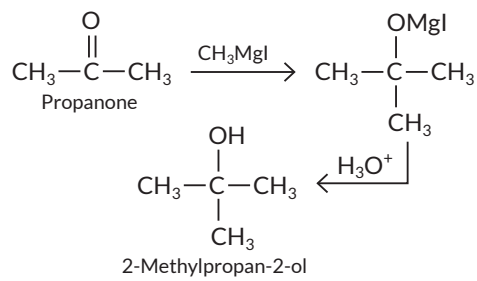
$\xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$

19. (d) : Iodoform test is given by the compound containing $CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3-\underset{OH}{\underset{|}{CH}}-$ group thus it cannot be given by pentan-3-one, *i.e.*,

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

20. (d) : Reactivity of ketones is less than aldehydes.

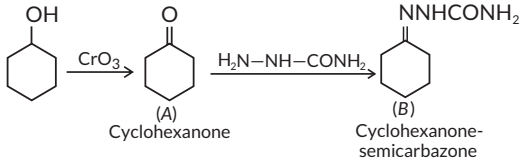
21. (d) : Aldehydes are easily oxidised to carboxylic acids on treatment with mild oxidising agents. Ketones are generally oxidised under vigorous conditions *i.e.*, strong oxidising agents and at elevated temperatures.

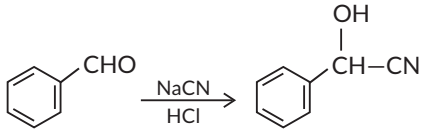
22. 

Concept Applied

➲ *R*MgX is called Grignard reagent. Its $R^-(R^-\overset{+}{M}gX)$ attacks on electrophilic centre of carbonyl compound $(\rangle C^+ - O^-)$

23. $CH_3-\underset{\text{Propanone (Acetone)}}{\overset{O}{\overset{\|}{C}}}-CH_3 \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_3} \xrightarrow[443\ K]{\text{Conc. } H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2}$

24. 

25. 

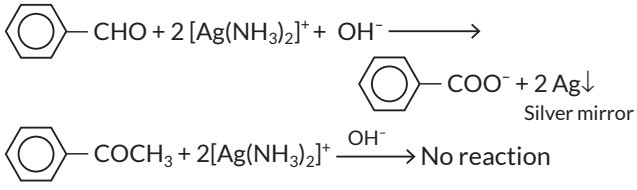
26. $\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_3} \xrightarrow{Cu/\Delta} \underset{\text{Propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$

27. Ethanal and propanal can be distinguished by iodoform test.

$\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{NaOI} HCOONa + \underset{\text{Yellow ppt.}}{CHI_3\downarrow}$

$\underset{\text{Propanal}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{NaOI}$ No reaction

28. Benzaldehyde and acetophenone can be distinguished by Tollens' test.



Alternative Method

➲ Acetophenone will give iodoform test whereas benzaldehyde will not.

$Ph-COCH_3 \xrightarrow{NaOI} \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + PhCOONa$

$Ph-CHO \xrightarrow{NaOI}$ No reaction

29. $CH_3COCl \xrightarrow{H_2,Pd\text{-}BaSO_4} \underset{\text{A (Ethanal)}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{H_2N-OH} \underset{\text{B (Ethanal oxime)}}{CH_3-C(=N-OH)-H}$

30. Propanal and butan-2-one can be distinguished by their reactions with Tollens' reagent.

$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} CH_3CH_2COO^- + \underset{\text{Silver mirror}}{2Ag\downarrow}$

$\underset{\text{Butan-2-one}}{CH_3CH_2COCH_3} + 2\,[Ag(NH_3)_2]^+ \xrightarrow{OH^-}$ No reaction

31. Lithium aluminium hydride ($LiAlH_4$).

Alternative Method

➲ Sodium borohydride ($NaBH_4$)

32. (i) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test.

$C_6H_5COOH + NaHCO_3 \longrightarrow \underset{\text{Effervescence}}{C_6H_5COONa + CO_2\uparrow + H_2O}$

$C_6H_5CHO + NaHCO_3 \longrightarrow$ No reaction

(ii) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} CH_3CH_2COO^- + \underset{\text{Silver mirror}}{2Ag\downarrow}$

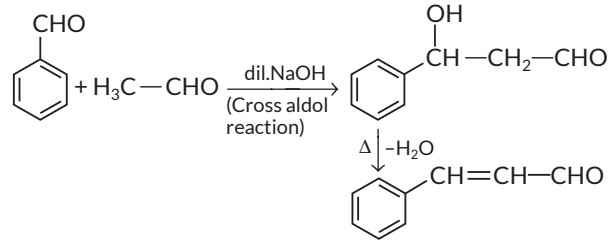
$\underset{\text{Propanone}}{CH_3COCH_3} + 2\,[Ag(NH_3)_2]^+ \xrightarrow{OH^-}$ No reaction

33. It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3, there are two electron releasing methyl groups attached to the carbonyl carbon that hinder the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO, there is only one methyl group attached to the carbonyl carbon.

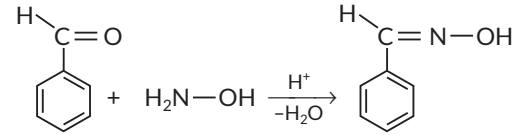
Concept Applied

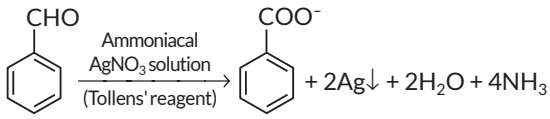
➲ Order of reactivity towards nucleophilic attack :
Acyl chlorides > Aldehydes > Ketones

34. (i)

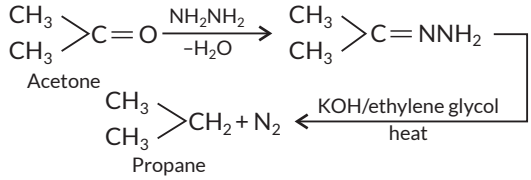


(ii)

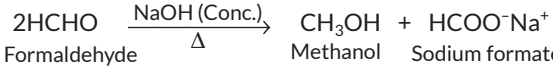


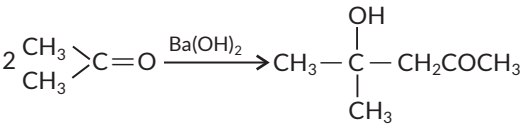
(iii) 

35. (a) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.

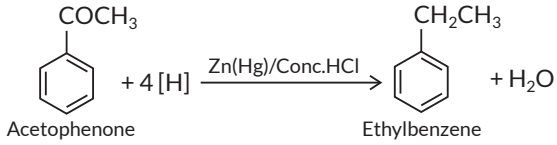


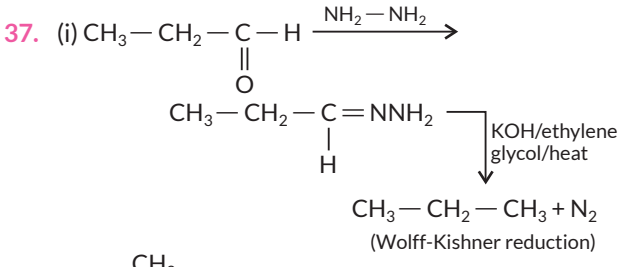
(b) **Cannizzaro reaction :** Aldehydes without α-hydrogen atom undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.



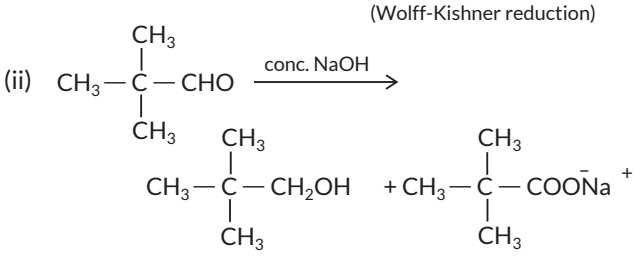
36. (i) 

4-Hydroxy-4-methylpentan-2-one

(ii) 

37. (i) 

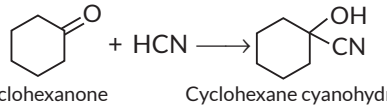
(Wolff-Kishner reduction)

(ii) 

(Cannizzaro reaction)

Answer Tips

- Aldehydes without any α-hydrogen undergo Cannizzaro reaction.

38. (a) 

(b) Butanal responds to Fehling test and silver mirror test but butan-2-one does not respond.

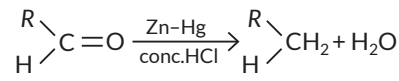
$CH_3CH_2CH_2CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2{-}CH_2COO^- + 2Cu_2O\downarrow$
Red-brown ppt.

$CH_3CH_2COCH_3 + 2Cu^{2+} + 5OH^- \longrightarrow$ No reaction

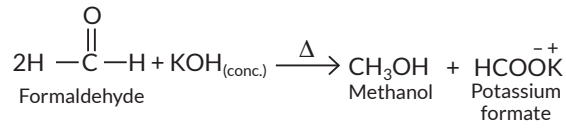
Alternative Method

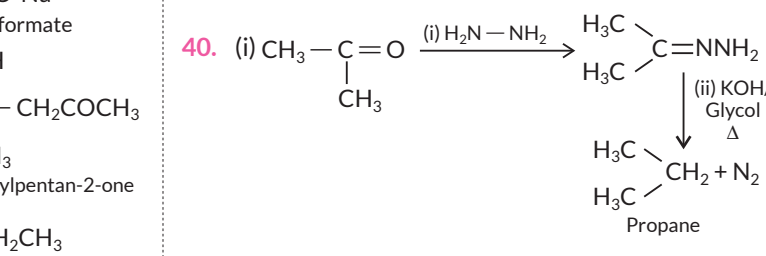
- Butanal and butan-2-one can also be distinguished by Tollens' test (given by aldehydes) and iodoform test (given by methyl ketones, $-COCH_3$).

39. (i) **Clemmensen reduction :**

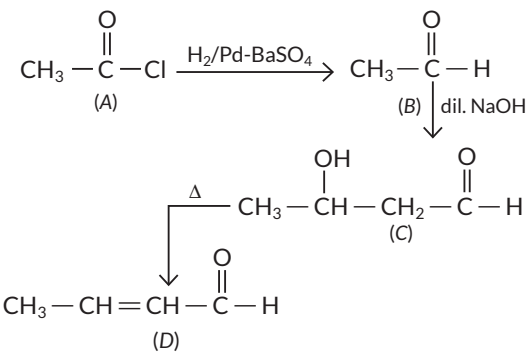


(ii) **Cannizzaro reaction :**

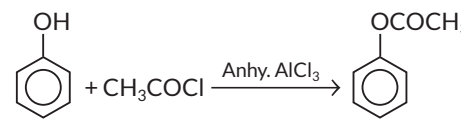


40. (i) 

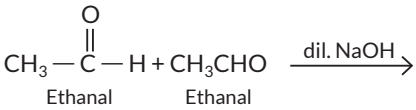
(ii) $C_6H_5{-}CO{-}CH_3 \xrightarrow{NaOH/I_2} CHI_3\downarrow + C_6H_5COO^-Na^+$
Iodoform

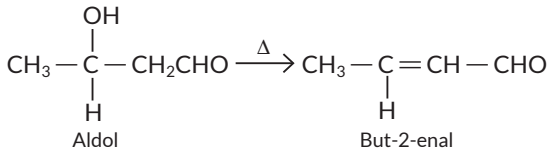
41. 

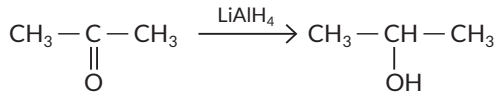
42. (i) **Acetylation :** Introduction of acetyl group $\left(-\overset{\overset{O}{\|}}{C}-CH_3\right)$ in alcohols, phenols or amines is called acetylation.

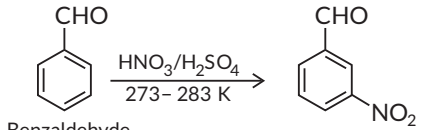


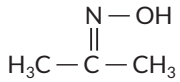
(ii) **Aldol condensation :** Two molecules of an aldehyde or ketone having at least one α-hydrogen atom condense in the presence of a dilute alkali to give β-hydroxyaldehyde or β-hydroxyketone which upon heating gives α,β-unsaturated aldehyde or ketone.

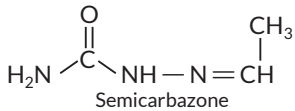


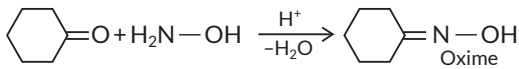


43. (i) 

(ii) 

44. (i) 

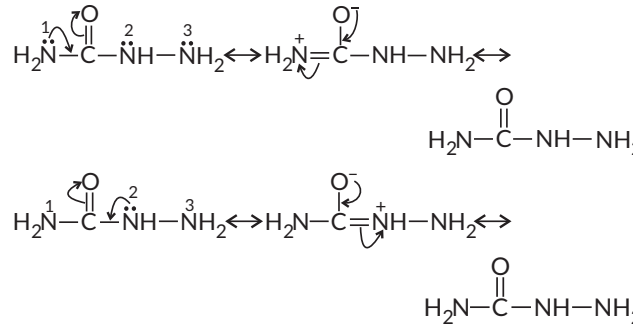
(ii) 

45. (i) 

(ii) $2C_6H_5CHO + \text{conc. NaOH} \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$

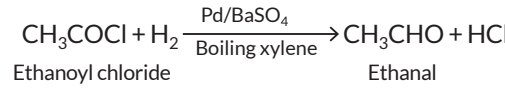
46. (i) It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3 there are two electron releasing methyl groups attached to the carbonyl carbon that hinder the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO, there is only one methyl group attached to the carbonyl carbon.

(ii) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.

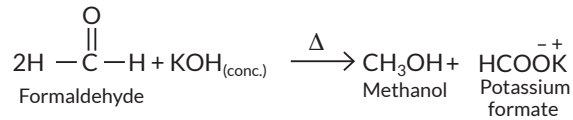


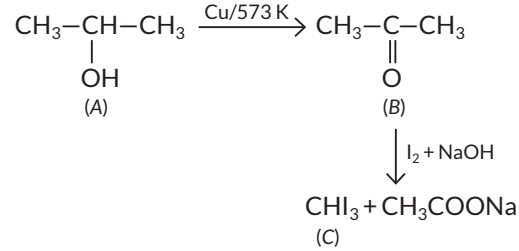
Lone pairs of N-1 and N-2 are involved in conjugation with $>C=O$ group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

47. (i) **Rosenmund's reduction :**



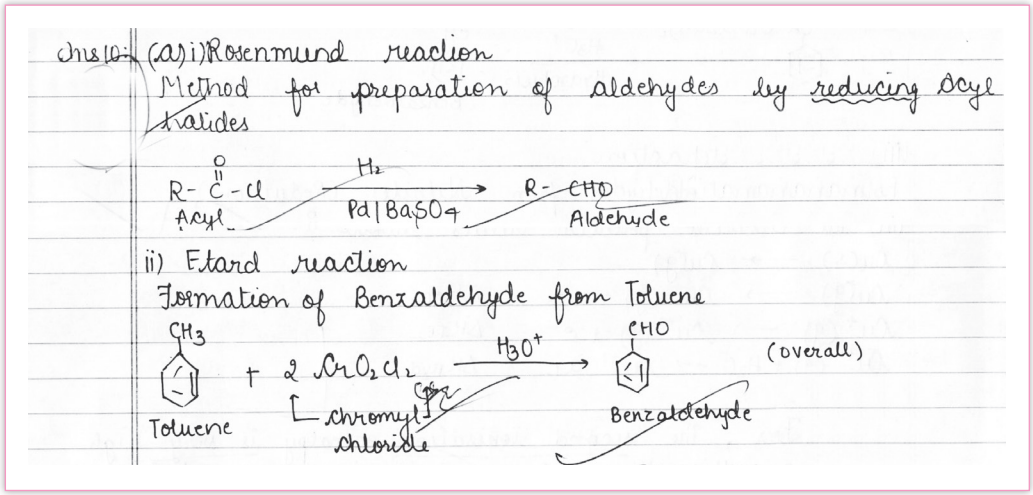
(ii) **Cannizzaro reaction :**

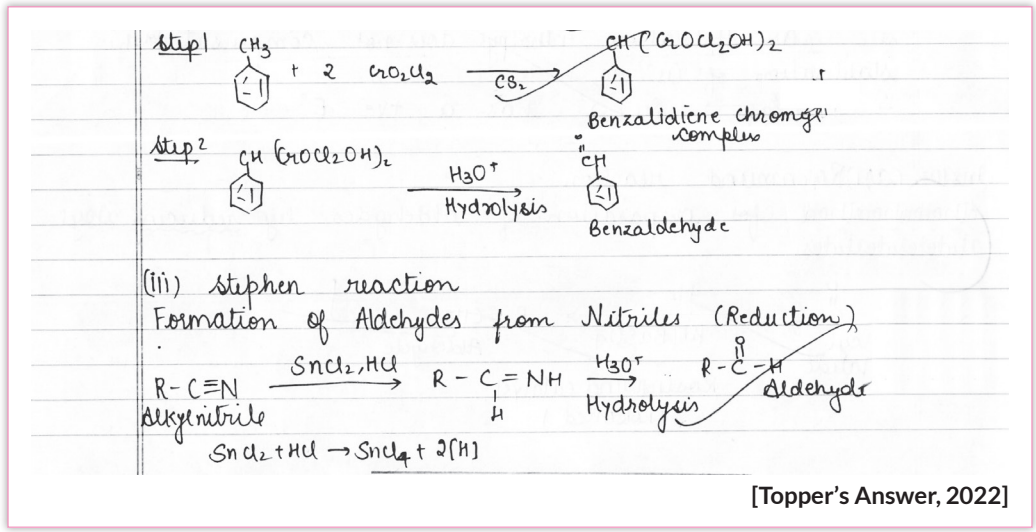


48. 

A having molecular formula (C_3H_8O) on reaction with Cu at 573 K results in formation of ketone (*B*). (*B*) does not reduce Fehling's solution but will form yellow precipitate of iodoform due to presence of $\left(CH_3-\overset{\overset{O}{\|}}{C}-\right)$ group.

49.





[Topper's Answer, 2022]

50. (i) Generally ketones are less reactive towards nucleophilic addition reaction because the +*I*-effect of alkyl groups makes carbonyl carbon less electrophilic as compared tos aldehydes that have only one alkyl group attached to carbonyl carbon. Moreover, the nucleophile attacks over ketones is restricted due to steric hinderance. So, acetaldehyde will undergo nucleophilic addition faster than propanone.

(ii) Fehling's reagent is a combination of two separate solutions, Fehling solution A and Fehling solution B. Fehling solution A is blue - coloured solution of copper sulphate, ($CuSO_4$). Fehling solution B is colourless aqueous solution of sodium potassium tartarate ($KNaC_4H_4O_6.4H_2O$), also known as Rochelle salt in alkaline medium.

(iii) $H_3C-CH=O$ (Ethanal) $+ H_2N-NH-C(=O)-NH_2 \longrightarrow H_3C-C(H)=N-NH-C(=O)-NH_2$ (Semicarbazone)

51. (i) $CH_3-C(=O)-CH_3$ (Propanone) $\xrightarrow{CH_3MgBr} CH_3-C(OMgBr)(CH_3)-CH_3 \xrightarrow{H_3O^+} CH_3-C(OH)(CH_3)-CH_3$ (2-Methylpropan-2-ol)

(ii) Ethanal $\xrightarrow{H^+}$ $\xrightarrow{HO-C_2H_5}$ $\xrightarrow{H^+}$ $\xrightarrow{C_2H_5OH}$ $H_5C_2O(H)(CH_3)C-OC_2H_5$

(iii) $2H-C(=O)-H + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOO^-K^+$
Formaldehyde — Methanol — Potassium formate

52. As the compound forms 2,4-DNP derivative, hence it is an aldehyde or ketone. It does not reduce Tollens' reagent, hence it is a ketone, not aldehyde. It gives positive iodoform test, hence it is a methyl ketone, *i.e.*, it contains $CH_3-C(=O)-$ group.

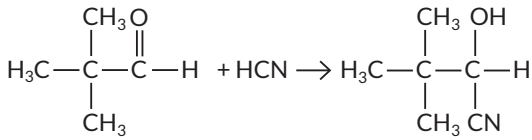
(i) Therefore '*X*' must be $CH_3-C(=O)-CH_2-CH_2-CH_3$ *i.e*, 2-pentanone

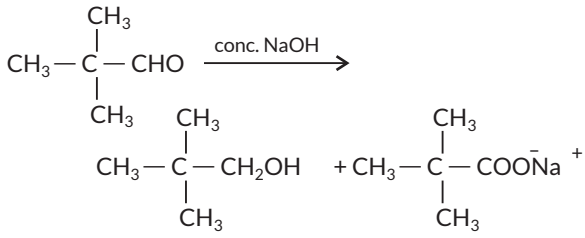
$CH_3-C(=O)-CH_2-CH_2-CH_3 \xrightarrow[\Delta]{\text{Conc. } HNO_3} CH_3COOH + CH_3CH_2COOH$
Ethanoic acid — Propanoic acid

(ii) $CH_3-C(=O)-CH_2-CH_2-CH_3 + H_2NNH-C_6H_3(NO_2)_2 \xrightarrow{H^+} CH_3-CH_2-CH_2-C(CH_3)=NNH-C_6H_3(NO_2)_2$

(iii) $CH_3-C(=O)-CH_2-CH_2-CH_3 \xrightarrow[NaOH]{I_2} CHI_3\downarrow + CH_3CH_2CH_2COONa + NaOH$

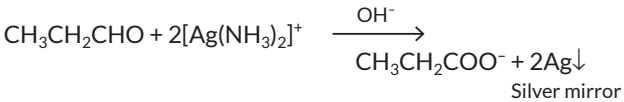
53. (i) $H_3C-C(CH_3)(CH_3O)-C(=O)-H + H_3C-C(=O)-CH_3 \xrightarrow[H^+]{\text{dilute NaOH}} H_3C-C(CH_3)(CH_3)-C(H)(OH)-CH_2-C(=O)-CH_3$

(ii) 

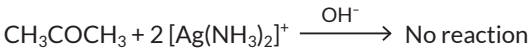
(iii) 

(Cannizzaro reaction)

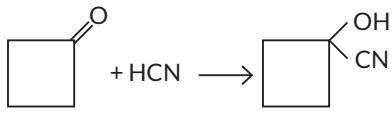
54. (a) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

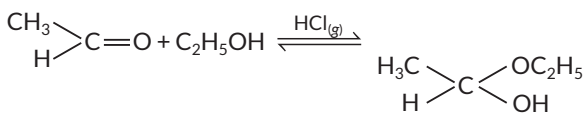


Silver mirror

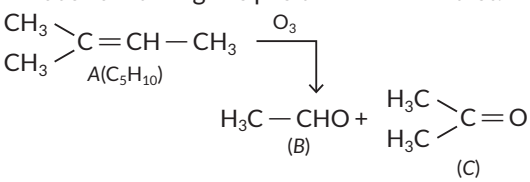


Propanone

(b) (i) 

(ii) 

55. As compound *B* gives positive Fehling's test so it is an aldehyde and as it gives positive iodoform test so it is acetaldehyde. Compound *C* does not give Fehling's solution test, so it is a ketone which could be acetone because acetone gives positive iodoform test.



A(C_5H_{10})

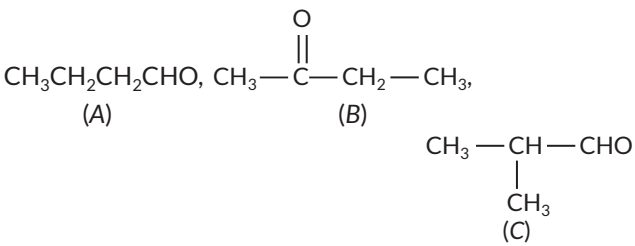
(B) *(C)*

Concept Applied

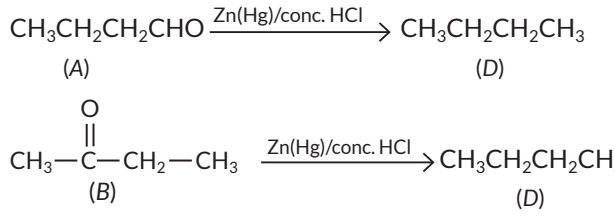
➲ Aldehydes give positive Fehling test while ketones do not.

56. (a) As (*A*) and (*C*) give positive Tollens' test thus these two should be aldehyde while (*B*) should be a ketone (does not give Tollens' test) with $-\overset{\overset{O}{\|}}{C}-CH_3$ group (as it gives positive iodoform test).

Three isomers are

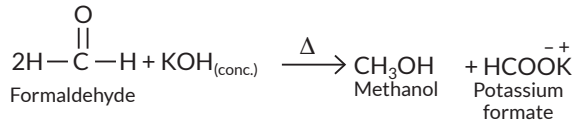


(A) *(B)* *(C)*

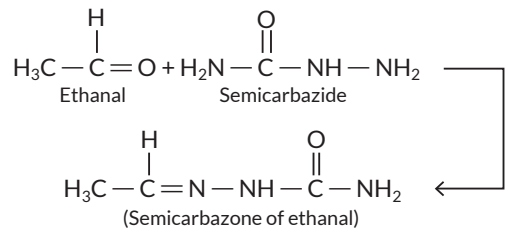


(b) Out of (*A*), (*B*) and (*C*) isomers, (*B*) is least reactive towards addition of HCN.

57. (a) **Cannizzaro reaction :**



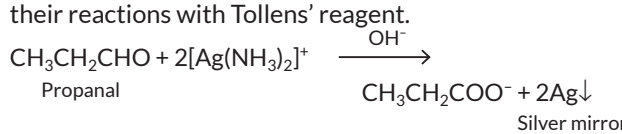
Formaldehyde Methanol Potassium formate

(b) 

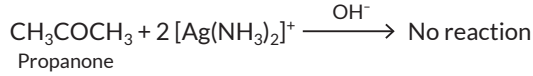
Ethanal Semicarbazide

(Semicarbazone of ethanal)

(c) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

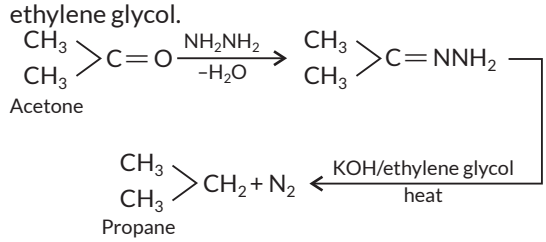


Propanal Silver mirror



Propanone

58. (a) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.

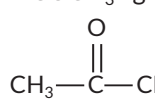


Acetone Propane

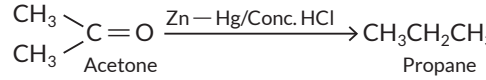
(b) Increasing order of reactivity towards nucleophilic addition reaction :

$C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$

(c) Formula of compounds *A* and *B* is C_3H_6O, *B* forms yellow precipitate of iodoform. Hence, *B* must contain $-COCH_3$ group. Therefore, compound '*B*' must be



A does not give iodoform test and it is functional isomer of *B* thus, it may be CH_3CH_2CHO.

59. (i) 

Acetone Propane

(ii) $(CH_3)_2C{=}O + H_2N{-}NHCONH_2 \xrightarrow{H^+} (CH_3)_2C{=}N{-}NHCONH_2$

Acetone semicarbazone

(iii) $(CH_3)_2C{=}O + CH_3MgBr \longrightarrow (CH_3)_2C(OMgBr)CH_3 \xrightarrow{H_3O^+} (CH_3)_2C(OH)CH_3$

2-Methylpropan-2-ol

60. (i) $CH_3CHO \xrightarrow{Zn-Hg/Conc.\ HCl} CH_3{-}CH_3$

(ii) $2CH_3CHO \xrightarrow{dil.\ NaOH} CH_3{-}CH(OH){-}CH_2{-}CHO$

(iii) $CH_3CHO \xrightarrow{H_2/Ni} CH_3{-}CH_2{-}OH$

61. (i) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.

$(CH_3)_2C{=}O \xrightarrow[-H_2O]{NH_2NH_2} (CH_3)_2C{=}NNH_2 \xrightarrow[heat]{KOH/ethylene\ glycol} (CH_3)_2CH_2 + N_2$

Acetone → Propane

(ii) **Aldol condensation :** Two molecules of an aldehyde or ketone having at least one α-hydrogen atom condense in the presence of a dilute alkali to give β-hydroxyaldehyde or β-hydroxyketone which upon heating gives α,β-unsaturated aldehyde or ketone.

CH_3CHO (Ethanal) + CH_3CHO (Ethanal) $\xrightarrow{dil.\ NaOH}$ $CH_3{-}CH(OH){-}CH_2{-}CHO$ (Aldol) $\xrightarrow{\Delta}$ $CH_3{-}CH{=}CH{-}CHO$ (But-2-enal)

(iii) **Cannizzaro reaction :**

$2HCHO + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOO^-K^+$

Formaldehyde → Methanol + Potassium formate

62. (i) $CH_3CHO + HCN \longrightarrow CH_3{-}CH(OH){-}CN$

(ii) $CH_3CHO + H_2NOH \longrightarrow CH_3{-}CH{=}N{-}OH$

(iii) $2CH_3CHO \xrightarrow{dil.\ NaOH} CH_3{-}CH(OH){-}CH_2{-}CHO$

63. (a) (i) **Rosenmund's reduction :**

$CH_3COCl + H_2 \xrightarrow[Boiling\ xylene]{Pd/BaSO_4} CH_3CHO + HCl$

Ethanoyl chloride (Acetyl chloride) → Ethanal (Acetaldehyde)

(ii) **Cannizzaro reaction :**

$2HCHO + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOO^-K^+$

Formaldehyde → Methanol + Potassium formate

(b) $CH_3CH_2CH_2{-}CO{-}CH_3$ will give iodoform test because it contains acetyl group.

$CH_3CH_2CH_2COCH_3 \xrightarrow{NaOI} CHI_3\downarrow + CH_3CH_2CH_2COONa$

Iodoform (Yellow ppt.)

64. (i) $CH_3{-}CHO + CH_3MgBr \xrightarrow{H_3O^+} CH_3{-}CH(OH){-}CH_3$

(ii) $CH_3CHO \xrightarrow[Conc.\ HCl]{Zn-Hg} CH_3{-}CH_3$

(iii) $CH_3{-}CHO + C_6H_5CHO \xrightarrow{dil.\ NaOH} C_6H_5{-}CH(OH){-}CH_2CHO$

65. (i) (1) $CH_3{-}CHO$ (Ethanal) $\xrightarrow{dil.\ NaOH}$ $CH_3{-}CH(OH){-}CH_2{-}CHO \xrightarrow{\Delta} CH_3{-}CH{=}CH{-}CHO$

But-2-en-1-al

(2) CH_3CH_2COOH (Propanoic acid) $\xrightarrow[(ii)\ H_2O]{(i)\ Cl_2,\ Red\ P} CH_3CH(Cl)COOH$

2-Chloropropanoic acid

(ii) As compound *B* gives positive Fehling's test so it is an aldehyde and as it gives positive iodoform test so it is acetaldehyde. Compound *C* does not give Fehling's solution test. So it is a ketone which could be acetone because acetone gives positive iodoform test.

$(CH_3)_2C{=}CH{-}CH_3$ (*A* (C_5H_{10})) $\xrightarrow{O_3}$ $H_3C{-}CHO$ (*B*) + $(H_3C)_2C{=}O$ (*C*)

66. (i) Only those aldehydes which do not have an α-hydrogen atom undergo self-oxidation and reduction reaction on treatment with concentrated alkali. In this reaction, one molecule of aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

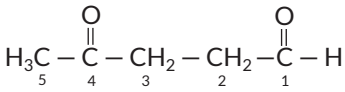
$\underbrace{HCHO}_{Formaldehyde} + HCHO \xrightarrow[\Delta]{conc.\ KOH} CH_3OH + HCOOK$

Methanol + Potassium formate

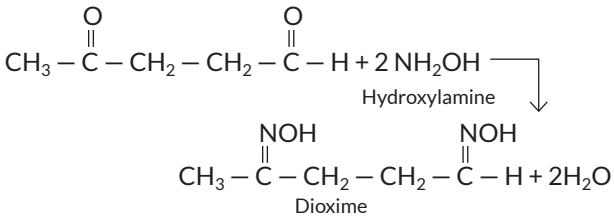
(ii) The boiling points of aldehydes and ketones are lower than that of corresponding carboxylic acids because they are not associated with intermolecular hydrogen bonding, whereas carboxylic acids are associated with intermolecular H-bonding.

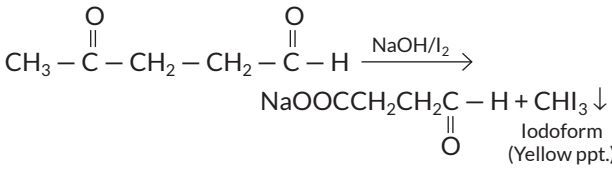
(iii) The organic compound '*A*' when treated with hydrazine ($NH_2 - NH_2$) followed by heating with NaOH and glycol forms *n*-pentane. This suggests that compound '*A*' must be a carbonyl compound. The molecular formula of '*A*' suggests that it must have two carbonyl groups, out of which one is an aldehyde.

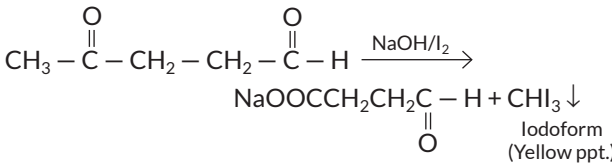
Thus, the expected structure of compound '*A*' is

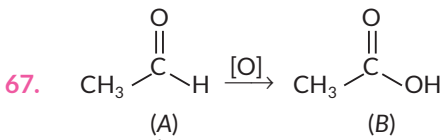


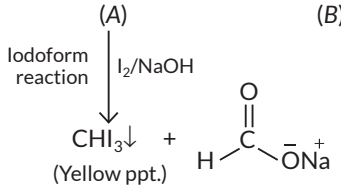
Pent-4-oxo-1-al

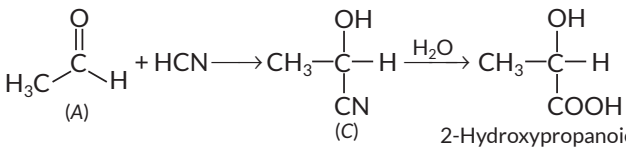






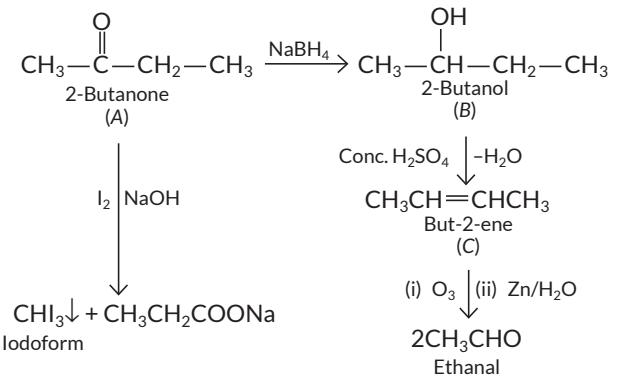
67. 





68. (a) As (*A*) forms 2, 4-DNP derivative, hence it is an aldehyde or ketone. Since it does not reduce Tollens' reagent, hence it is a ketone (*A*). As it gives iodoform reaction, hence it is a methyl ketone, *i.e.*, contains $CH_3-\overset{O}{\overset{\|}{C}}-$ group.

Therefore, (*A*) must be $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ *i.e.*, 2-butanone.



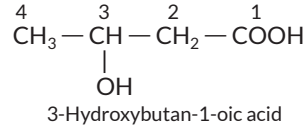
(b) (i) Unlike aldehydes, ketones do not contain any hydrogen atom attached to $>C=O$ group and hence they cannot be oxidised without the cleavage of some carbon-carbon bonds. Thus oxidation of propanal is easier than propanone.

(ii) Due to $-I$ effect of the carbonyl group of aldehydes and ketones, it withdraws electrons from the adjacent carbon-carbon bond. This makes α-carbon electron deficient. The α-carbon in turn, withdraws electrons from the C_α—H bonds. As a result, the electron density in C_α—H bond decreases. Hence, the α-hydrogens are weakly held and can be easily abstracted by strong bases giving enolate anions which are stabilised by resonance.

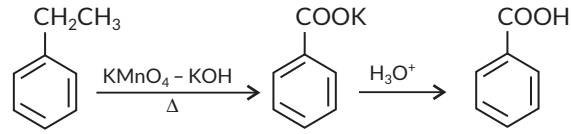
Concept Applied

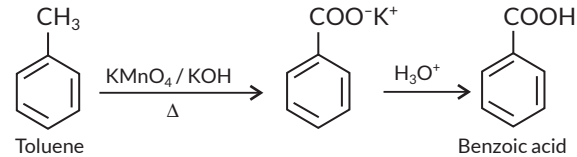
➲ Carbonyl group ($>C=O$) exerts $-I$ effect and hence stabilise the anion formed after removal of H^+.

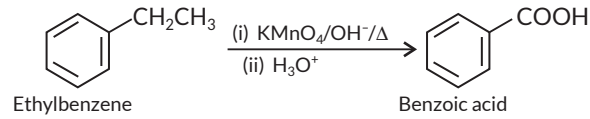
69. (a)

70. 

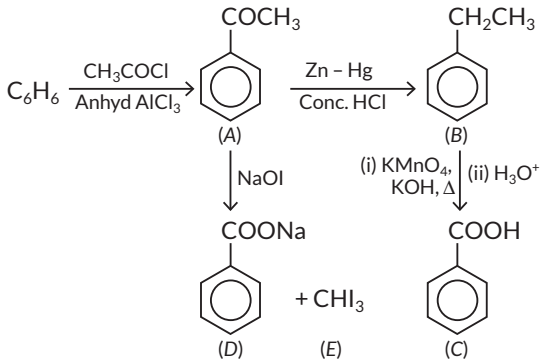
3-Hydroxybutan-1-oic acid

71. 

72. 

73. 

74. Alkaline potassium permanganate ($KMnO_4$, KOH)

75. 

76. Increasing order of boiling point :
$CH_3CHO < C_2H_5OH < CH_3COOH$

77. **(b):** As $pK_a \propto \frac{1}{\text{acidity}}$

$O_2N - CH_2 - COOH$ will be most acidic due to presence of strong electron withdrawing group *i.e.*, $-NO_2$.

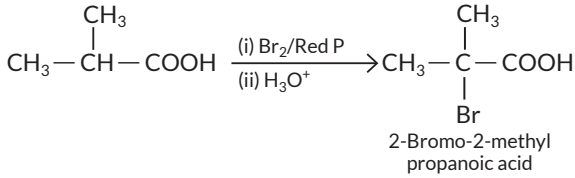
78. **(a):** Carboxylic acid does not undergo Friedel-Crafts reaction because (i) the carboxyl group is strongly deactivating and (ii) the catalyst $AlCl_3$ gets bonded to the carboxyl group strongly.

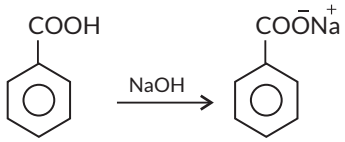
79. **(c) :** Due to presence of electron withdrawing group (—COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

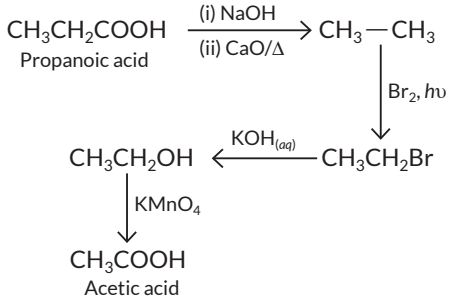
80. (a) Acidic strength increases as $-I$ effect (F > Cl) of substituents increases, so the order of acidity is :
$CH_3COOH < ClCH_2COOH < FCH_2COOH$.

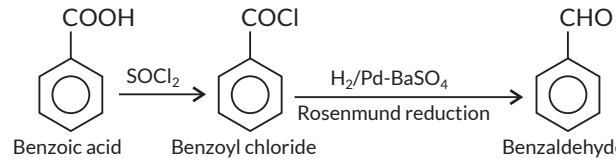
(b) Alcohols have higher boiling point as compared to aldehydes or alkanes of comparable molecular mass due to the presence of intermolecular hydrogen bonding in them.

Boiling point order : $CH_3CH_2CH_3 < CH_3CHO < CH_3CH_2OH$

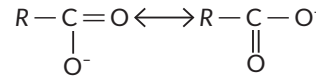
81. 

82. 

83. 

84. 

85. The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :



86. Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ whereas ethyl benzoate does not react.

$$C_6H_5COOH + NaHCO_3 \longrightarrow \underset{\text{Effervescence}}{C_6H_5COONa + CO_2\uparrow + H_2O}$$

$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No reaction}$$

87. Add Tollens' reagent to formic acid and warm. Silver mirror is formed.

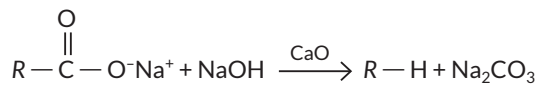
$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+ + 2OH^- \xrightarrow{\text{Warm}} \underset{\text{Silver mirror}}{2Ag\downarrow} + CO_2 + 2NH_3 + 2NH_4OH$$

Acetic acid does not give this test.

88. $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$

89. $CH_3-COOH \xrightarrow{PCl_5} CH_3-COCl + POCl_3 + HCl$

90. **Decarboxylation :** Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.



91. Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.

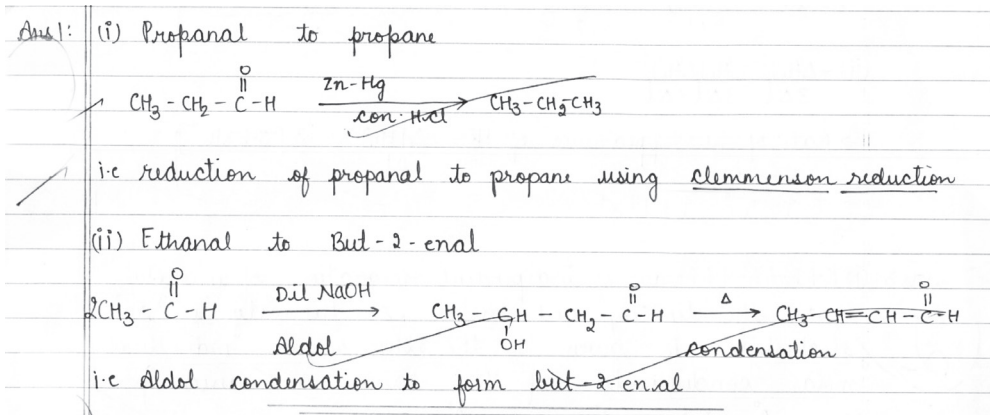
$$C_6H_5COOH + NaHCO_3 \longrightarrow \underset{\text{Effervescence}}{C_6H_5COONa + CO_2\uparrow + H_2O}$$

$$C_6H_5OH + NaHCO_3 \longrightarrow \text{No reaction}$$

92. **Hell-Volhard-Zelinsky reaction :** Carboxylic acids react with chlorine or bromine in the presence of phosphorous to give compounds in which α-hydrogen atom is replaced by halogen atom.

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Chloroacetic acid}}{ClCH_2-COOH} + HCl$$

93.



[Topper's Answer, 2022]

(iii) Ethanoic acid to ethanamide

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + NH_3 \rightarrow CH_3COO\bar{N}H_4^+ \xrightarrow[-H_2O]{\Delta} \underset{\text{Ethanamide}}{CH_3CONH_2}$$

94. (i) $\underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow[\text{Pd-BaSO}_4]{H_2} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$

(ii) $CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-\underset{H}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-CH_2CHO$

(iii) $CH_3COOH \xrightarrow[\text{Red P}]{Cl_2} ClCH_2-COOH$

95. (i) $C_6H_5COCH_3 < CH_3COCH_3 < C_6H_5CHO < CH_3CHO$

The reactivity towards nucleophilic addition reactions decreases as the steric hindrance and +*I* effect of the alkyl groups increases. Due to +*R* effect of the benzene ring, the aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.

(ii) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

Acidic strength of carboxylic acid is increased by the presence of electron with drawing groups while decreased by the presence of electron donating groups. Inductive effect decreases rapidly with distance.

(iii) $CH_3CHO < C_2H_5OH < CH_3COOH$

Alcohols have higher boiling points than aldehydes of similar molecular weight due to the presence of H–bonding in alcohols. Carboxylic acids have higher boiling points than alcohols because of more extensive association of carboxylic acid molecules through inter-molecular hydrogen bonding.

96. (i) Due to presence of electron withdrawing group (—COOH) in aromatic carboxylic acids, they do not undergo Friedel—Crafts reaction.

(ii) Unlike aldehydes, ketones do not contain any hydrogen atom attached to $>C=O$ group and hence, they cannot be oxidised without the cleavage of some carbon-carbon bonds. Thus, oxidation of aldehydes is easier than ketones.

97. (i) Greater the number of alkyl groups attached to the carbonyl group, greater is the electron density on the carbonyl carbon and hence, lower is its reactivity towards nucleophilic addition reactions.

The +*R* effect of the benzene ring increases the electron density on the carbonyl group thereby repelling the nucleophiles. Hence, aromatic aldehydes are less reactive than the corresponding aliphatic aldehydes.

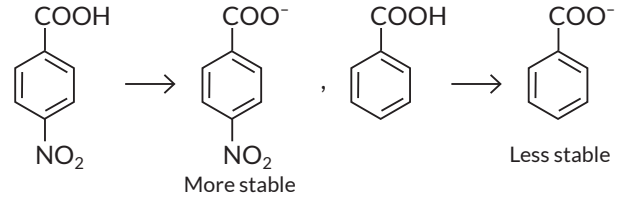
So, the increasing order of reactivity is

$\underset{\text{Benzaldehyde}}{C_6H_5CHO} < \underset{\text{Propanal}}{CH_3CH_2CHO}$

(ii) The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compounds. It is due to resonance stabilisation of carboxylate ion :

$$R-\underset{O^-}{\overset{|}{\underset{|}{C}}}=O \longleftrightarrow R-\underset{O}{\overset{||}{C}}-O^-$$

(iii) 4-Nitrobenzoic acid is a stronger acid than benzoic acid because conjugate base obtained from the 4-nitrobenzoic acid is more stable in comparison of conjugate base obtained from benzoic acid. This is due to –*R* effect of electron withdrawing nitro group.



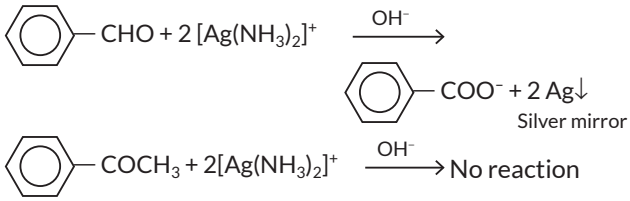
98. (i) $F-CH_2-COOH$ is stronger acid as compared to $H_3C-COOH$ due to –*I* effect of fluorine that stabilises the conjugate base formed after the loss of H^+.

(ii) Alcohols have higher boiling points than aldehydes of similar molecular weight due to the presence of H–bonding in alcohols. Carboxylic acids have higher boiling points than alcohols because of more extensive association of carboxylic acid molecules through inter-molecular hydrogen bonding.

Order of boiling point :

$CH_3-CHO < CH_3CH_2OH < H_3C-COOH$

(iii) Benzaldehyde and acetophenone can be distinguished by Tollens' test. Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' test.



99. (a) $C_6H_5COOH < FCH_2COOH < NO_2CH_2COOH$

Electron withdrawing groups increase the stability of the carboxylate ion by dispersing the negative charge and hence increase the acidity of the substituted acid. The effect of given substituents follows the order: Ph < F < NO_2.

(b) $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}(=O)-H$

1-Butanal

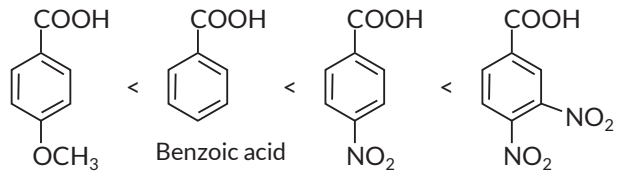
100. (a) Generally aldehydes are more reactive than ketones towards nucleophilic addition reactions because aldehydes are less sterically hindered and possess low electron density on carbonyl carbon due to the presence of single alkyl substituent with the carbonyl group.

So, order of reactivity is :

Butanone < Propanone < Propanal < Ethanal.

(b) Acidic strength of acid is increased by the presence of electron withdrawing groups at *–o* and *–p* positions of the ring, while electron donating groups decrease its acidic strength.

Order of acidity :



4-Methoxy benzoic acid | Benzoic acid | 4-Nitro-benzoic acid | 3, 4-Dinitro-benzoic acid

101. (a) Due to presence of electron withdrawing group (—COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

(b) Due to presence of strong electron withdrawing group (—NO_2), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore, pK_a value is lower.

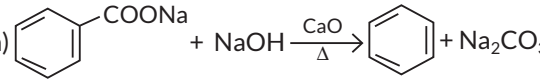
102. (i) **Hell-Volhard-Zelinsky reaction :** Carboxylic acids react with chlorine or bromine in the presence of phosphorous to give compounds in which α-hydrogen atom is replaced by halogen atom.

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Chloroacetic acid}}{ClCH_2-COOH} + HCl$$

(ii) **Decarboxylation :** Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.

$$R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

103. (a)

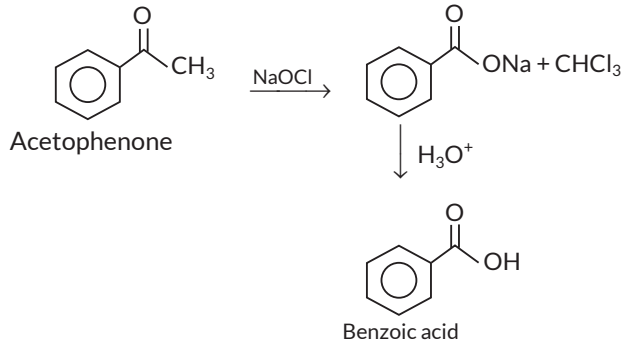


Sodium benzoate | Benzene

(b) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution.

Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.

104. (i) Acetophenone to benzoic acid :



Acetophenone | Benzoic acid

(ii) Ethanoic acid to 2-hydroxyethanoic acid.

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[H_2O]{Cl_2/\text{Red P}} \underset{\text{2-Chloroethanoic acid}}{Cl-CH_2-COOH} \xrightarrow{NaOH} \underset{\text{2-Hydroxyethanoic acid}}{HO-CH_2-COOH}$$

105. (a) $CH_3COOH \xrightarrow{Cl_2/\text{ Red P}} \underset{Cl}{CH_2COOH}$

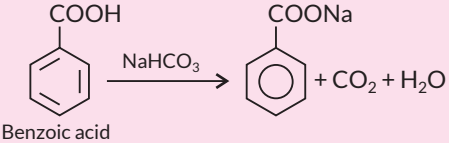
(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow \underset{\text{Silver mirror}}{C_6H_5COO^-} + 2Ag\downarrow + 4NH_3 + 2H_2O$$

Benzoic acid does not give this test.

Alternative Method

➲ **Sodium Bicarbonate test :** Benzoic acid reacts with sodium bicarbonate to liberate CO_2.

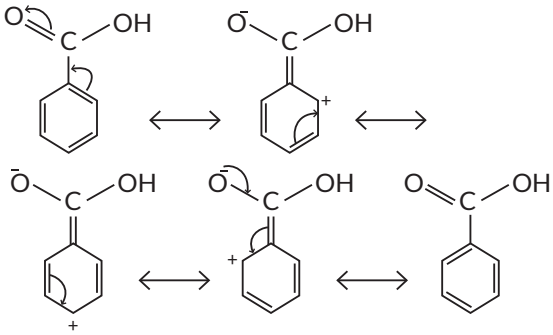


Benzoic acid

C_6H_5CHO does not give this test.

106. Chloroacetic acid has lower pK_a value than acetic acid; 'Cl' in chloroacetic acid shows *–I* effect, it creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier. Hence, chloroacetic acid is stronger than acetic acid.

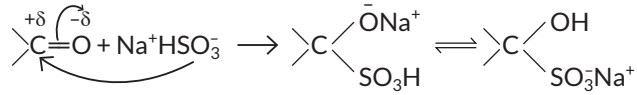
107. (i) Resonance structures of benzoic acid;



Resonance structures show that carboxylic acid group present in benzoic acid acts as a ring deactivating and *meta* directing group.

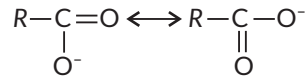
(ii) Sodium hydrogensulphite ($NaHSO_3$) adds on aldehydes and ketones to give addition products.

$$NaHSO_3 \longrightarrow Na^+ + HSO_3^-$$

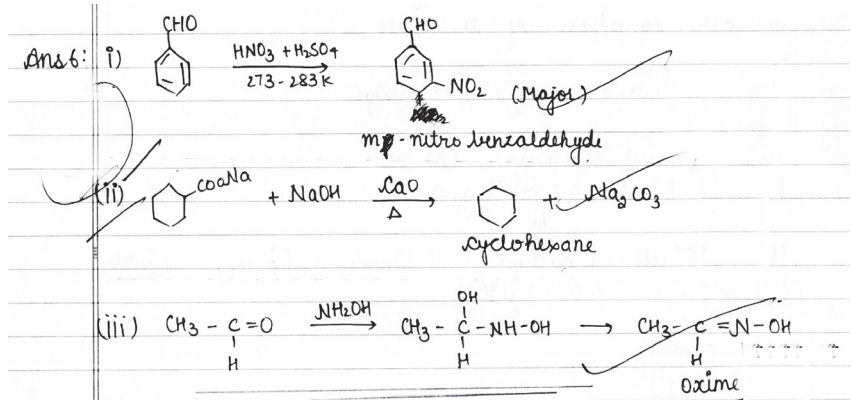


Most of the aldehydes give product in good yield. Most of the ketones give very poor yield due to steric hindrance in the crystalline solid and highly soluble in water. These can be converted back to the original carbonyl compound by reaction with dilute mineral acids or alkali. Therefore, this reaction is used for the separation and purification of aldehydes and ketones.

(iii) The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compounds. It is due to resonance stabilisation of carboxylate ion :

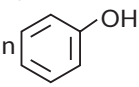


108.

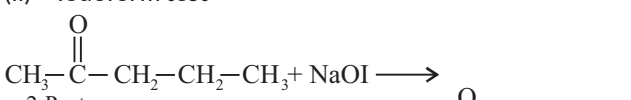


[Topper's Answer, 2022]

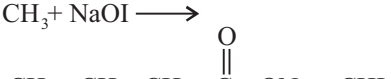
109. (i) (I) $F-CH_2COOH > CH_3COOH$

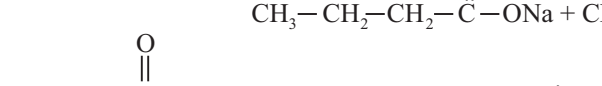
(II) CH_3COOH is stronger than 

(ii) Iodoform test



2-Pentanone

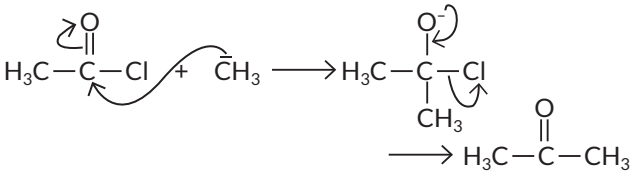




3-Pentanone

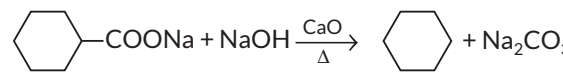
110. (i) $2H_3C-\overset{O}{\overset{\|}{C}}-Cl + (CH_3)_2Cd \longrightarrow 2H_3C-\overset{O}{\overset{\|}{C}}-CH_3$

Mechanism :

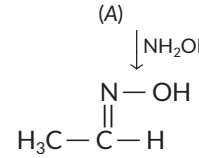


(ii) $CH_3CH_2CHO \xrightarrow[\text{Conc. HCl}]{Zn(Hg)} CH_3CH_2CH_3 + H_2O$

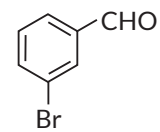
This reaction is an example of Clemmensen reduction.

(iii) 

111. (a) (i) $CH_3CN \xrightarrow[(2)\ H_2O]{(1)\ AlH(i\text{-}Bu)_2} CH_3CHO$ (*A*)

$\xrightarrow{NH_2OH/H^+}$ 

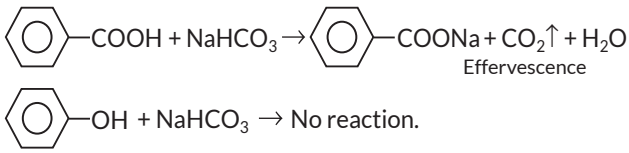
Ethanal oxime (*B*)

(ii) 

IUPAC name : 3-Bromobenzaldehyde

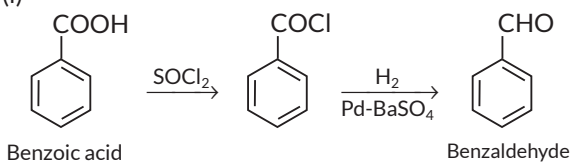
(iii) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give brisk effervescence of CO_2 with $NaHCO_3$ but

phenol will not give because it is weaker acid than benzoic acid.



OR

(b) (i)



(ii) $H_3C-CH_2-CH_2-OH \xrightarrow[\text{Oxidation}]{K_2Cr_2O_7/H_2SO_4} H_3C-CH_2-COOH \xrightarrow{\text{(i) } Br_2/\text{Red P, (ii) } H_2O} H_3C-\underset{Br}{CH}-COOH$

Propan-1-ol — 2-Bromopropanoic acid

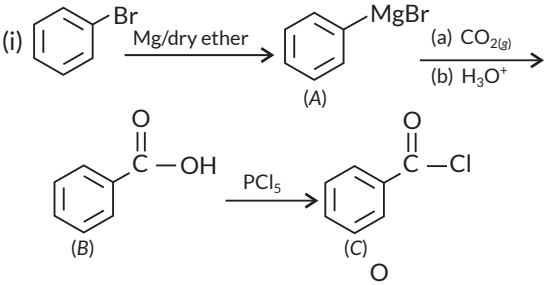
(iii) $CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{|} + CH_3CHO \xrightarrow{\text{dil. NaOH}}$

Ethanal + Ethanal

$CH_3-\underset{H}{\overset{OH}{\overset{|}{C}}}-CH_2CHO \xrightarrow{\Delta} CH_3-\underset{H}{C}=CH-CHO$

Aldol — But-2-enal

112. (i)



(ii) $CH_3-C\equiv N \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } SnCl_2/HCl} CH_3-\overset{O}{\overset{\|}{C}}-H$ (A)

(A) $\xrightarrow{\text{dil. NaOH}}$ $CH_3CH=CH-\overset{O}{\overset{\|}{C}}-H \xleftarrow{\Delta} CH_3-\underset{H}{\overset{OH}{\overset{|}{C}}}-\underset{H}{\overset{H}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-H$

(C) — (B)

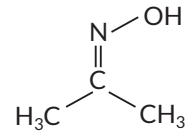
Concept Applied

➲ $H_3C-C\equiv N \xrightarrow{SnCl_2/HCl} H_3C-CH=NH\cdot HCl$

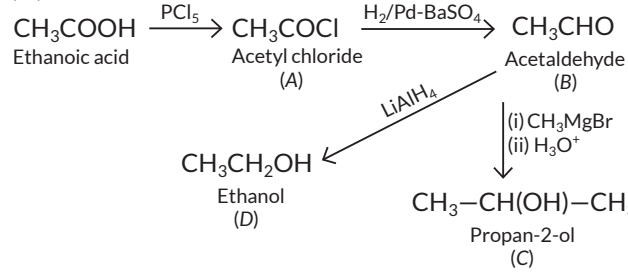
113. (i) (1) Butanone and butanal can be distinguished by Tollens' test as aldehyde will give positive Tollens' test while ketone does not give any reaction.

(2) Ethanal and ethanoic acid can be distinguished by sodium bicarbonate test. Carboxylic acid gives brisk effervescence with $NaHCO_3$ while aldehyde does not form any effervescence.

(ii) Oxime of acetone is an organic compound with formula $(CH_3)_2CNOH$. It is simplest example of ketoxime. The structure



(iii)



114. (i) Sodium bicarbonate test can be used to distinguish between ethanal and ethanoic acid as a brisk effervescence of CO_2 gas is observed when ethanoic acid reacts with $NaHCO_3$, whereas ethanal does not react with $NaHCO_3$.

$CH_3COOH_{(l)} + NaHCO_{3(s)} \rightarrow CH_3COONa_{(aq)} + CO_{2(g)}\uparrow + H_2O_{(l)}$

(ii) The α-hydrogens of aldehydes and ketones are acidic in nature due to the presence of carbonyl group that has a strong electron withdrawing effect. Another reason is the resonance stabilisation of the anion formed after the removal of α-hydrogen.

(iii) The given organic compound '*A*' with molecular formula, $C_4H_8O_2$ is an ester that undergoes acid hydrolysis to give carboxylic acid and alcohol.

$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow[\text{Hydrolysis}]{aq.H_2SO_4} \underset{'B'}{CH_3COOH} + \underset{'C'}{C_2H_5OH}$

('A')

$\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[\text{alkaline } KMnO_4]{\text{acidified } K_2Cr_2O_7} \underset{\text{Ethanoic acid}}{CH_3COOH}$

(C) (B)

Now, sodium salt of '*B*' is sodium acetate (CH_3COONa) which reacts with soda lime to give methane as shown:

$CH_3COONa + NaOH \xrightarrow[633\ K, \Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$

(1) *A* is $CH_3COOC_2H_5$
B is CH_3COOH
C is C_2H_5OH

(2) Out of '*B*' and '*C*', *i.e.*, ethanoic acid and ethanol, the former has a higher boiling point as due to the formation of a dimer, the van der Waals force increases, causing an increase in the boiling point. The dimer is formed due to the presence of H-bonding between carbonyl oxygen and acidic hydrogen.

115. (a) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

The reactivity towards nucleophilic addition reactions decreases as the steric hindrance and +*I* effect of the alkyl groups increases. Due to +*R* effect of the benzene ring, the aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.

(b) Tollens' reagent test :

$$CH_3CHO + [Ag(NH_3)_2]^{2+} \xrightarrow{3OH^-} CH_3COO^- + 2Ag\downarrow + 2H_2O + 4NH_3$$

$$\underset{\text{Propanone}}{CH_3COOH} \xrightarrow[\text{reagent}]{\text{Tollens'}} \text{No reaction}$$

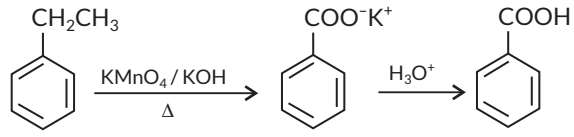
(c) The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :

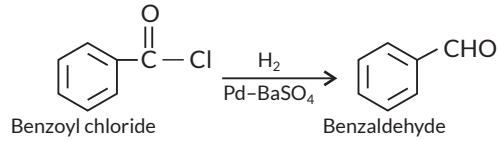
$$R-C(=O)-O^- \longleftrightarrow R-C(-O^-)=O$$

(d) (i) The acidity of α-hydrogens of aldehydes and ketones is due to the –*I* effect of the carbonyl group which weakens the C_α–H bond and due to the resonance stabilisation of the resulting enolate anion.

(ii) $2C_6H_5CHO + \text{conc. } NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$

OR

(i) 

(ii) 

116. (a) Aldehydes having α-H undergo aldol condensation. Thus, HCHO and C_6H_5CHO will not undergo aldol condensation, only CH_3CHO will undergoes aldol condensation.

(b) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} CH_3CH_2COO^- + 2Ag\downarrow$$

Silver mirror

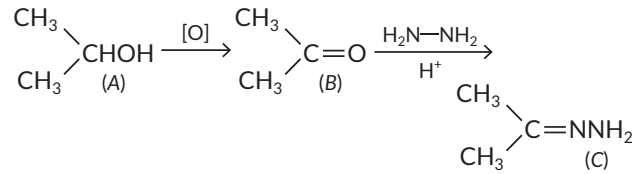
$$\underset{\text{Propan-2-one}}{CH_3COCH_3} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} \text{No reaction}$$

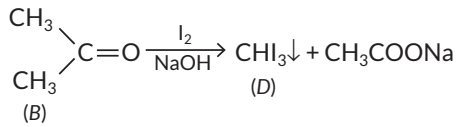
(c) $CH_2=CH-CH_2OH \xrightarrow[273-295K]{CrO_3-H_2SO_4,\ (CH_3)_2CO-H_2O} CH_2=CH-CHO$

Jones reagent is a solution of CrO_3 in H_2SO_4 in aqueous acetone. It is used to oxidise allylic and benzylic 1° and 2° alcohols to corresponding aldehyde.

(d) (i) As '*B*' gives negative Tollens' test, hence it is a ketone. '*B*' reacts with NaOH and I_2, so it is a methyl ketone.

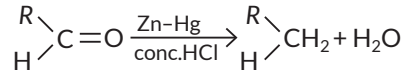
Hence '*A*' is a 2° alcohol.





OR

(ii) (I) **Clemmensen reduction :**

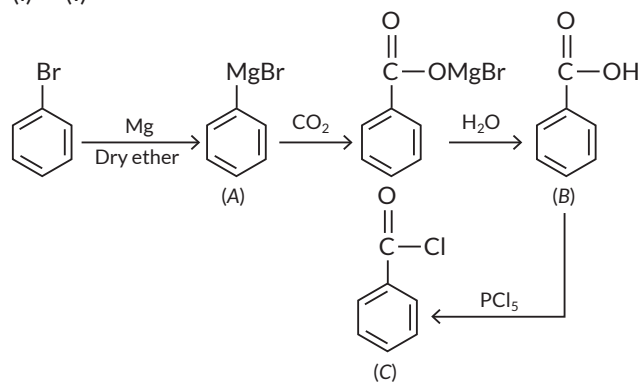


(II) **HVZ reaction :**

$$RCH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}} R-CHX-COOH \quad (X = Cl \text{ or } Br)$$

117.

(i) (I)



(II) $CH_3-CH_2OH \xrightarrow{CrO_3} CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-CH(OH)-CH_2-CHO \xrightarrow{\Delta} CH_3-CH=CH-CHO$

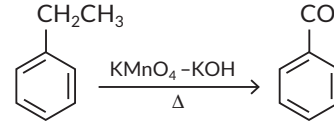
(*A*) (*B*) (*C*)

(ii) (I) Ethanol (having CH_3CHOH- group) give iodo form test while benzaldehyde will not.

$$CH_3CH_2OH \xrightarrow[\Delta]{I_2/NaOH} CHI_3\downarrow + HCOONa$$

(II) Acetic acid reacts with $NaHCO_3$ to give effervescence while ethanol acid do not

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + H_2O + CO_2\uparrow$$

118. (i) (I) 

(II) $CH_2=CH-CHO \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_2=CH-CH_2-OH$

(ii) $CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{N-OH}{||}}{C}}$

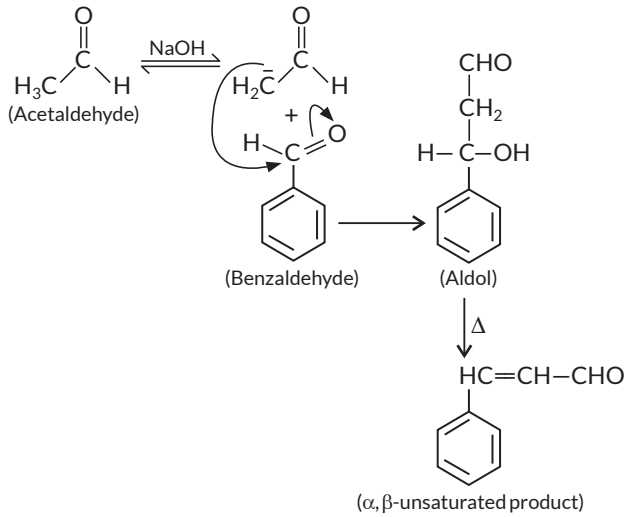
(iii) The carbonyl group in $-COOH$ is inert and does not show nucleophilic addition reaction like carbonyl compounds. It is due to resonance stabilisation of carboxylate ion :

$$R-\underset{\underset{O^-}{|}}{\overset{\overset{O}{||}}{C}}=O \longleftrightarrow R-\underset{\underset{O}{||}}{\overset{\overset{O^-}{|}}{C}}$$

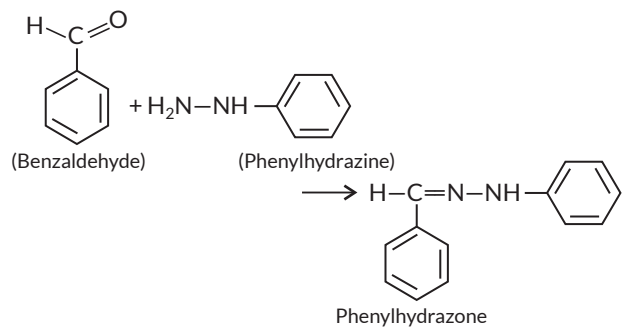
(iv) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

The reactivity towards nucleophilic addition reactions decreases as the steric hindrance and $+I$ effect of the alkyl groups increases. Due to $+R$ effect of the benzene ring, the aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.

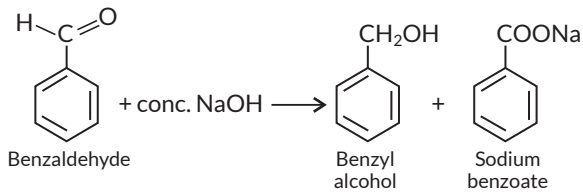
119. (a) (i) When benzaldehyde reacts with CH_3CHO in presence of dilute NaOH, aldol condensation reaction occurs in which α, β-unsaturated product is formed.



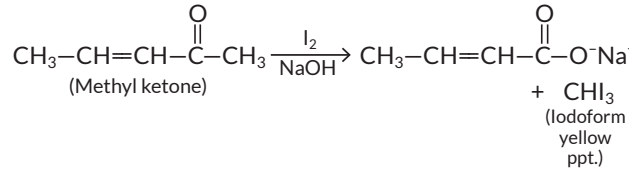
(ii) Benzaldehyde reacts with phenylhydrazine to form phenyl hydrazone.



(iii) Benzaldehyde reacts with conc. NaOH to form benzyl alcohol and sodium benzoate.



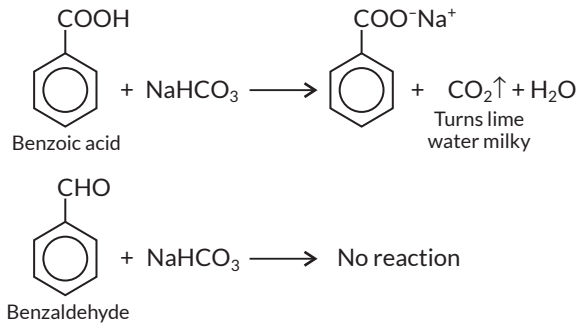
(b) (i) $CH_3CH=CHCOCH_3$ and $CH_3CH_2COCH=CH_2$ can be distinguished by iodoform test.



$CH_3CH_2-\overset{\overset{O}{||}}{C}-CH=CH_2 \xrightarrow{I_2/NaOH}$ No yellow ppt.

Pent-3-en-2-one will give yellow precipitate of iodoform on reaction with I_2 and NaOH due to presence of $(CH_3-\overset{\overset{O}{||}}{C}-)$ group.

(ii) Benzoic acid and benzaldehyde can be distinguished by $NaHCO_3$ (sodium bicarbonate). Benzoic acid turns lime water milky due to release of CO_2 while benzaldehyde does not undergo such reaction.



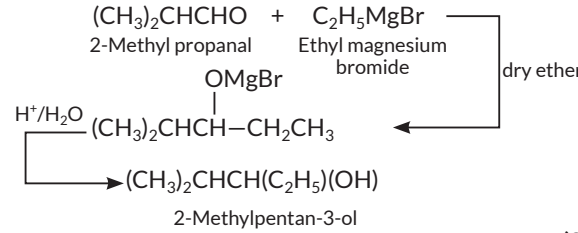
CBSE Sample Questions

1. (a) **(1)**

2. (c) : 2,4-DNP test is given by both aldehydes and ketones.

Fehling's, Tollens' and Cannizzaro reaction is shown by aldehydes only. **(1)**

3.

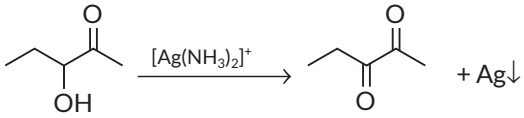


(2)

4. (a) The alpha hydrogen atoms are acidic in nature due to presence of electron withdrawing carbonyl group which makes the anion resonance stabilised. In

aldol condensation, alkali reacts with α-hydrogen of aldehyde or ketone to form β-hydroxyaldehyde (aldol) or β-hydroxyketones (ketol), respectively. **(1)**

(b) Tollens' reagent is a weak oxidising agent not capable of breaking the C—C bond in ketones . Thus, ketones cannot be oxidised by using Tollens' reagent except α-hydroxyketones.



(1)

5. Compound *A* is an alkene, on ozonolysis it will give carbonyl compounds. As both *B* and *C* have >C=O group, *B* gives positive Fehling's test so it is an aldehyde and it gives iodoform test so it has $H_3C-\overset{O}{\overset{\|}{C}}-$ group. This means the aldehyde is acetaldehyde. *C* does not give Fehling's test, so it is a ketone. It gives positive iodoform test showing that it is a methyl ketone means it has $H_3C-\overset{O}{\overset{\|}{C}}-$ group.

Compound *A* (C_5H_{10}) on ozonolysis gives *B* (CH_3CHO) and *C*(CH_3COR). So '*C*' is CH_3COCH_3.

$$CH_3CH{=}C(CH_3)_2 \xrightarrow[(ii)\ Zn/H_3O^+]{(i)\ O_3} CH_3CHO + CH_3COCH_3$$ **(1/2)**

$$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + \underset{\text{(red ppt.)}}{Cu_2O} + 3H_2O$$

$CH_3COCH_3 + 2Cu^{2+} + 5OH^- \longrightarrow$ No reaction **(1/2)**

$CH_3CHO + 3I_2 + 3NaOH \longrightarrow \underset{\text{(Yellow ppt.)}}{CHI_3} + 3HI + HCOONa$ **(1/2)**

$CH_3COCH_3 + 3I_2 + 3NaOH \rightarrow \underset{\text{(Yellow ppt.)}}{CHI_3} + CH_3COONa + 3HI$

A = $CH_3CH{=}C(CH_3)_2$ **(1/2)**

B = CH_3CHO **(1/2)**

C = CH_3COCH_3 **(1/2)**

6. *A* is an alkene while '*B*' gives Silver mirror test so, *B* is an aldehyde with $-CH_3$ group.

As '*C*' gives yellow precipitate so, *C* is a methyl ketone.

(a) *A* : $CH(CH_3){=}C(CH_3)_2$; *B* : CH_3CHO; *C* : $O{=}C(CH_3)_2$ **(1)**

(b) $\underset{(B)}{CH_3CHO} + [Ag(NH_3)_2]^+ + OH^- \longrightarrow CH_3COO^- + Ag + NH_3 + H_2O$ **(1)**

(c) $CH_3COCH_3 + NaOH + I_2 \longrightarrow CHI_3 + CH_3COONa$ **(1)**

(d) $\underset{(C)}{CH_3COCH_3} + \underset{(B)}{CH_3CHO}$

$\downarrow Ba(OH)_2$

$(CH_3)_2C(OH)CH_2COCH_3 + CH_3CH(OH)CH_2CHO +$
$(CH_3)_2C(OH)CH_2CHO + CH_3CH(OH)CH_2COCH_3$

$\downarrow$ heat

$(CH_3)_2C{=}CHCOCH_3 + CH_3CH{=}CHCHO +$
$(CH_3)_2C{=}CHCHO + CH_3CH{=}CHCOCH_3$ **(2)**

OR

(a) *A* : CCl_3COOH *B* : CH_3COOH **(1)**

(b) $\underset{(B)}{CH_3COOH} \xrightarrow[(ii)\ H_2O]{(i)\ Red\ P/Cl_2} \underset{(A)}{CCl_3COOH},$ **(1)**

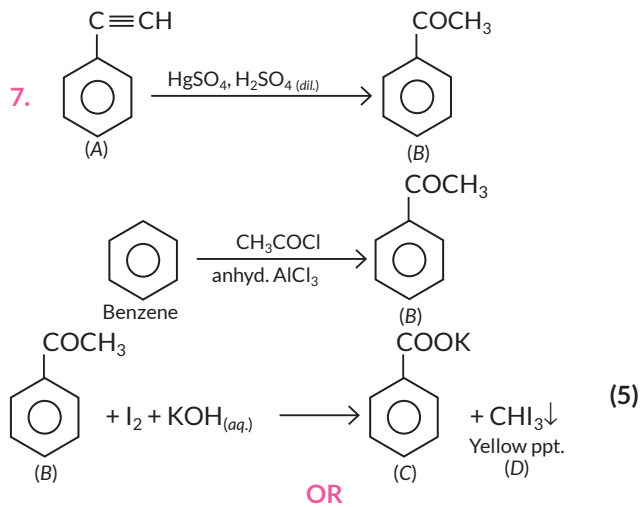
It is known as Hell Volhard Zelinsky reaction.

(c) $CH_3COCl \xrightarrow{H_2O} CH_3COOH$ **(1)**

(d) *A* will be more acidic due to presence of 3 Cl groups (electron withdrawing groups) which increase acidity of carboxylic acid.

(e) $\underset{(B)}{CH_3COOH} \xrightarrow{(i)\ NaOH,\ CaO\ (ii)\ heat} \underset{\text{(Methane)}}{CH_4} + Na_2CO_3$ **(1)**

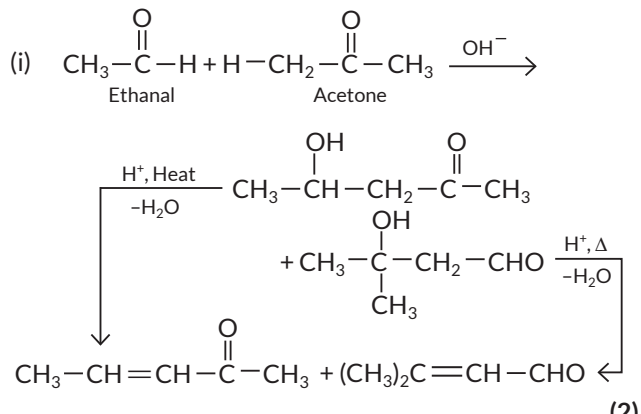
7.



(5)

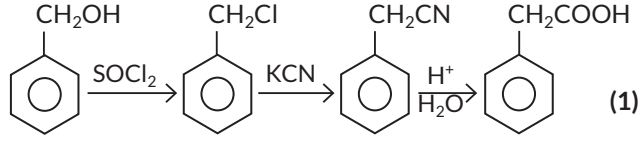
OR

(i)



(2)

(ii) (a)

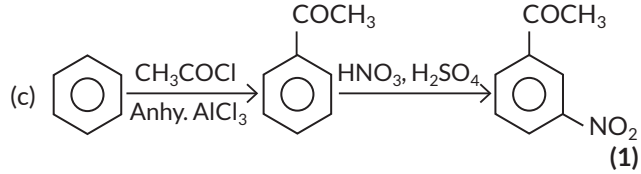


(1)

(b) $CH_3COCH_3 \xrightarrow{H_2/Pd} CH_3CH(OH)CH_3$

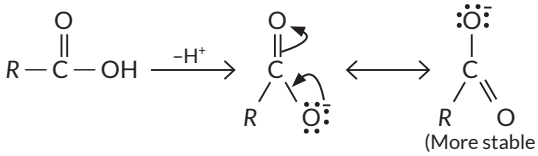
$\xrightarrow{H_2SO_4} CH_3CH{=}CH_2$ **(1)**

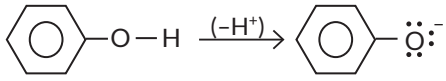
(c)



(1)

8. (b) : Carboxylic acids are more acidic than phenols. This can be explained on the basis of stability of conjugate base obtained after removal of H^+ from acid or phenol.





(Less stable phenoxide ion)

The conjugate base of carboxylic acid is stablized by two equivalent structures in which negative charge delocalises on more electronegative oxygen atom whereas in case of phenol, the negative charge delocalises on one oxygen atom and less electronegative carbon atom making less stable. Therefore, carboxylic acids are more acidic than phenol.

The (—OH) group present on phenol makes it *ortho* and *para*-directing as the carbocation formed is comparatively more stable at *o*- and *p*-position rather than *meta*-postion. **(1)**

9. (a) Picric acid < Salicylic acid < Benzoic acid < Phenol.

Higher is the pK_a value lesser is the K_a value, then lesser is the acidic character. **(1)**

(b) Methyl *tert* - butyl ketone < Acetone < Acetaldehyde

(Reaction with NH_2OH is a nucleophilic addition reaction). **(1)**

(c) Ethanol < ethanoic acid < benzoic acid

Boiling point of carboxylic acids is higher than alcohols due to extensive hydrogen bonding. Further, among carboxylic acids, boiling point increases with increase in molar mass. **(1)**

Self Assessment

Case Based Questions (5 marks)

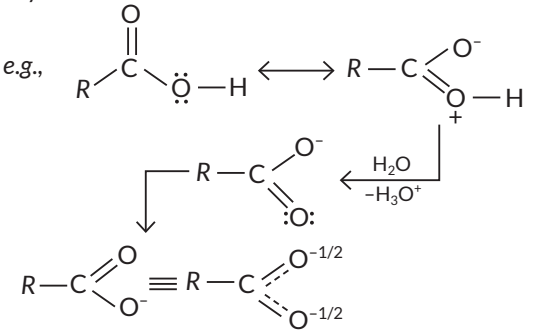
1. Read the passage given below and answer the following questions :

Carboxylic acids dissociate in water to give carboxylate ion and hydronium ion.

$RCOOH + H_2O \longrightarrow RCOO^- + H_3O^+$

The acidity of carboxyl group is due to the presence of positive charge on oxygen which liberates proton. The carboxylate ion formed is resonance stabilised.

e.g.,



Carboxylic acids are stronger acids than phenols. Electron withdrawing groups (EWG) increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of negative charge by inductive and/or resonance effects. Electron donating group (EDG) decrease the acidity by destabilising the conjugate base.

(i) Which of the following reactions is showing the acidic property of carboxylic acid?

(a) $2R-COOH + 2Na \longrightarrow 2R-COONa + H_2$

(b) $R-COOH + NaOH \longrightarrow R-COONa + H_2O$

(c) $2R-COOH + 2Na_2CO_3 \longrightarrow 2R-COONa + H_2O + CO_2\uparrow$

(d) All of these.

(ii) Which one of the following is the correct order of acidic strength?

(a) $CF_3COOH > CHCl_2COOH > HCOOH > C_6H_5CH_2COOH > CH_3COOH$

(b) $CH_3COOH > HCOOH > CF_3COOH > CHCl_2COOH > C_6H_5CH_2COOH$

(c) $HCOOH > C_6H_5CH_2COOH > CF_3COOH > CHCl_2COOH > CH_3COOH$

(d) $CF_3COOH > CH_3COOH > HCOOH > CHCl_2COOH > C_6H_5CH_2COOH$

(iii) The acidic strength of the given compounds follows the order :

I. $CH_3-CH=CH-COOH$

II. $CH_3-\ddot{O}-CH=CH-COOH$

III. CH_3-CH_2-COOH

(a) II > III > I (b) III > II > I

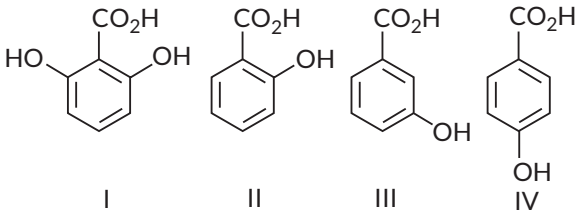
(c) II > I > III (d) I > II > III

(iv) Which of the following acids has the smallest dissociation constant?

(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH

(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

(v) The correct order of acidity for the following compounds is



I II III IV

(a) I > II > III > IV (b) III > I > II > IV

(c) III > IV > II > I (d) I > III > IV> II

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

2. **Assertion :** Formaldehyde is a planar molecule.
Reason : It contains sp^2 hybridised carbon atom.

3. **Assertion :** The α-hydrogen atom in carbonyl compounds is less acidic.
Reason : The anion formed after the loss of α-hydrogen atom is resonance stabilised.

Multiple Choice Questions (1 mark)

4. Benzophenone can be obtained by _____.

(a) benzoyl chloride + phenol + $AlCl_3$

(b) benzoyl chloride + diphenylcadmium

(c) benzoyl chloride + ethylmagnesium chloride

(d) benzene + carbon monoxide + $ZnCl_2$

5. CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished chemically by

(a) Benedict's test (b) Iodoform test

(c) Tollens' reagent test (d) Fehling's solution test.

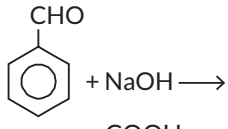
6. $(CH_3)_2CO \xrightarrow[HCl]{NaCN} A \xrightarrow{H_3O^+} B$

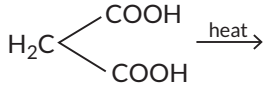
In the above sequence of reactions (*A*) and (*B*) are
(a) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)COOH$
(b) $(CH_3)_2C(OH)CN$, $(CH_3)_2C(OH)_2$
(c) $(CH_3)_2C(OH)CN$, $(CH_3)_2CHCOOH$
(d) $(CH_3)_2C(OH)CN$,$(CH_3)_2C{=}O$

7. The correct order of reactivity of aldehydes and ketones towards hydrogen cyanide is
(a) $CH_3COCH_3 > CH_3CHO > HCHO$
(b) $CH_3COCH_3 > HCHO > CH_3CHO$
(c) $CH_3CHO > CH_3COCH_3 > HCHO$
(d) $HCHO > CH_3CHO > CH_3COCH_3$

VSA Type Questions (1 mark)

8. Complete the following equations :

(i) 

(ii) 

9. Explain the Hell–Volhard–Zelinsky reaction.

10. The C — O bond length in *R*COOH is shorter than in *R* — OH. Give reason.

11. Acetic acid in vapour state has a molecular mass of 120. Why?

OR

Write the product obtained on reaction of benzene with CO/HCl in the presence of anhydrous $AlCl_3$.

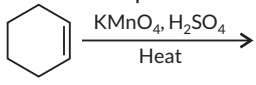
SA I Type Questions (2 marks)

12. Arrange the following in decreasing order of their acidic strength and give reason for your answer.
CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

13. What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH? Write the name of the reaction also.

14. Describe decarboxylation reaction by giving chemical equation.

15. Predict the product of the following reaction :



16. Arrange the following compounds in an increasing order of their property as indicated :
Acetaldehyde, acetone, methyl *tert*-butyl ketone (reactivity towards HCN)

OR

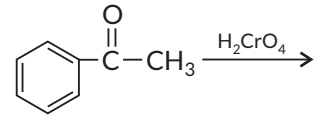
Why is there a large difference in the boiling points of butanal and butan-1-ol?

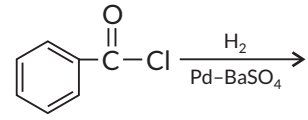
SA II Type Questions (3 marks)

17. Arrange the following compounds in an increasing order of their property as indicated :
(i) Benzoic acid, 3,4-dinitrobenzoic acid, 4-methoxybenzoic acid (acid strength)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$ (acid strength)

18. Write the mechanism of esterification of carboxylic acids.

19. Predict the products of the following reactions :

(i) 

(ii) 

20. An aliphatic compound '*A*' with a molecular formula of C_3H_6O reacts with phenylhydrazine to give compound '*B*'. Reaction of '*A*' with I_2 in alkaline medium on warming gives a yellow precipitate '*C*'. Identify the compounds *A*, *B* and *C*.

OR

Compound '*A*' was prepared by oxidation of compound '*B*' with alkaline $KMnO_4$. Compound '*A*' on reduction with lithium aluminium hydride gets converted back to compound '*B*'. When compound '*A*' is heated with compound '*B*' in the presence of H_2SO_4 it produces fruity smell of compound '*C*'. To which family the compounds '*A*', '*B*' and '*C*' belong to?

Case Based Questions (4 marks)

21. **Read the passage given below and answer the following questions :**

Aldehydes and ketones having acetyl group $\left(CH_3-\overset{\overset{O}{\|}}{C}-\right)$ are oxidised by sodium hypohalate (NaO*X*) or halogen and alkali ($X_2 + OH^-$) to corresponding sodium salt having one carbon atoms less than the carbonyl compound and give a haloform.

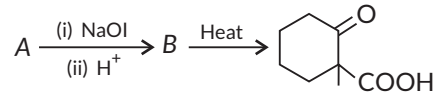
$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{or } X_2 + NaOH]{NaOX} R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{N}a + CHX_3$$

(*X* = Cl, Br, I)

Sodium hypoiodite (NaOI) when treated with compounds containing CH_3CO- group gives yellow precipitate of iodoform. Haloform reaction does not affect a carbon-carbon double bond present in the compound.

(i) Write the iodoform reaction of acetone.

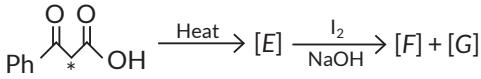
(ii) For the given reaction,



Identify the starting compound *A*.

(iii) An organic compound '*P*' has the molecular formula C_3H_6O. It undergoes iodoform test. Give the IUPAC name of *P*.

(iv) In the following reaction sequence,



(* implies ^{13}C labelled carbon)

What are the structures of *E*, *F* and *G*?

OR

Amongst propionaldehyde and *iso*-propyl alcohol which will give positive iodoform test.

LA Type Questions (5 marks)

22. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O. Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

23. An organic compound (*A*) on treatment with acetic acid in the presence of sulphuric acid produces an ester (*B*). (*A*) on mild oxidation gives (*C*). *C* with 50% KOH followed by acidification with dilute HCl generates (*A*) and (*D*). (*D*) with PCl_5 gives (*E*) which on reaction with ammonia gives methanamide. Identify the compounds *A*, *B*, *C* and *D*.

24. (a) Write the complete reaction for each of the following conversions stating the conditions necessary :
(i) Toluene to benzaldehyde
(ii) Aldehyde to acetal
(b) Describe the preparation of acetic acid from acetylene.
(c) How can the following be obtained from acetic acid :
(i) Acetaldehyde
(ii) Acetone?

25. Complete the following reactions.

(a) $CH_3CHBrCH(CH_3)CH_2CH_3 \xrightarrow[\Delta]{alc.\ KOH} A \xrightarrow{HBr} B \xrightarrow[ether]{Mg} C \xrightarrow[H_3O^+]{CO_2} D$

(b) $CH_3-CH_2-COOH \xrightarrow[H^+]{C_2H_5OH} A \xrightarrow[(ii)\ H_2O]{(i)\ C_6H_5MgBr} B \xrightarrow{\Delta} C \xrightarrow[[O]]{CrO_3} D$

OR

An alkene '*A*' (Mol. formula C_5H_{10}) on ozonolysis gives a mixture of two compounds '*B*' and '*C*'. Compound '*B*' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound '*C*' does not give Fehling's test but forms iodoform. Identify the compounds *A*, *B* and *C*. Write the reaction for ozonolysis and formation of iodoform from '*B*' and '*C*'.

Detailed SOLUTIONS

1. (i) (d) : All the reactions are showing the acidic properties of carboxylic acid. Carboxylic acid forms the sodium salts with all *i.e.*, alkali metals, NaOH and Na_2CO_3 and removes the acidic proton from the carboxylic acid.

(ii) (a): In general, greater the +*I* effect of the group attached to the carboxyl group, lesser will be the acidic strength and greater the −*I* effect of the group, greater will be acidic strength. As number of halogen atoms and electronegativity of halogen atom increases, acidic strength increases.

Thus, correct order of acidic strength is

$CF_3COOH > CHCl_2COOH > HCOOH > C_6H_5CH_2COOH > CH_3COOH$

(iii) (d)

(iv) (c): Stronger −*I* group attached closer to —COOH makes the acid stronger, *i.e.*, acid has the larger dissociation constant. —Br shows poor (−*I*) effect and also far away from —COOH group *i.e.*, option (c) has smallest dissociation constant.

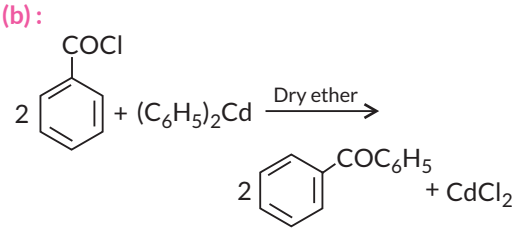
(v) (a): Due to *ortho*-effect, (I) and (II) are stronger acids than (III) and (IV). Due to two *ortho*-hydroxyl groups in (I), it is stronger acid than (II) due to H-bonding from both side. (III) is a stronger acid than (IV) because at *m*-position, —OH group cannot exert its +*R* effect but can only exert its −*I* effect while at *p*-position, —OH group exerts its strong +*R* effect.

Thus, the correct order of acidity is : I > II > III > IV

2. (a): Formaldehyde is a planar molecule because it contains sp^2 hybridised carbon atom.

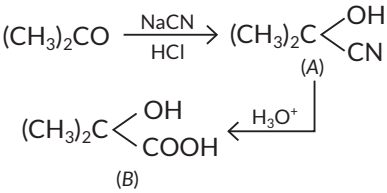
3. (d): The α-hydrogen atom in carbonyl compounds is more acidic.

4. (b) :

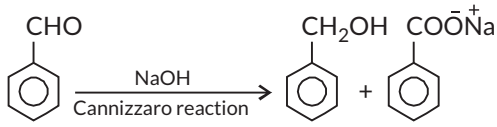


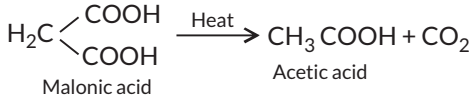
5. (b): Acetaldehyde, having CH_3CO- group undergo haloform reaction. Thus, CH_3CHO will give yellow precipitate with I_2 and NaOH but $C_6H_5CH_2CHO$ will not.

6. (a):



7. (d): Alkyl group attached to carbonyl carbon increases the electron density on the carbonyl carbon and lowers its reactivity towards nucleophilic addition reactions.
Also, as the number and size of alkyl group increases, the attack of nucleophile on the carbonyl group becomes more and more difficult due to steric hindrance.
Hence, the reactivity order will be :
$HCHO > CH_3CHO > CH_3COCH_3$

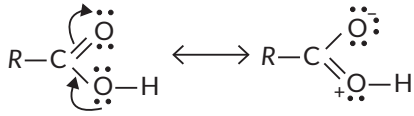
8. (i) 

(ii) 

9. Carboxylic acids having α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.

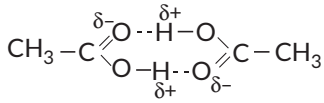
e.g., $RCH_2COOH \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2 + Red\ P} R-\underset{Cl}{\underset{|}{CH}}-COOH$
α-Chlorocarboxylic acid

10. Carboxylic acids show resonance which is not possible in alcohols.



Resonance structures show that the C — O bond of acid has some double bond character, hence is shorter in length.

11. Acetic acid exists as a dimer due to hydrogen bonding hence molecular mass is 120.



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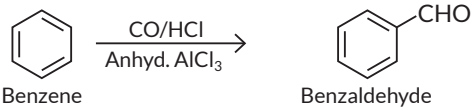
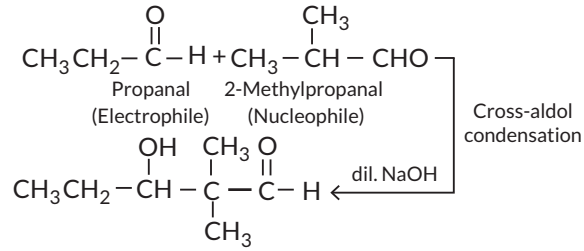
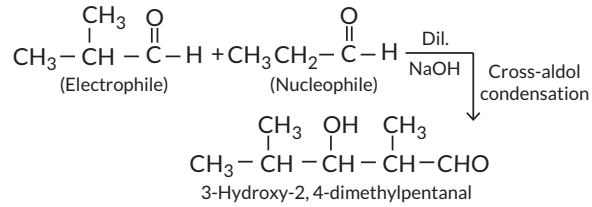
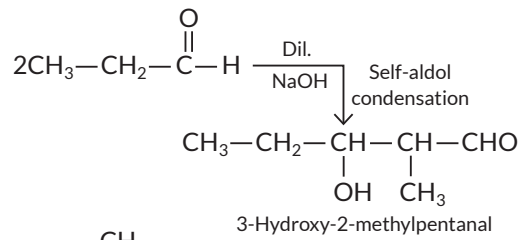


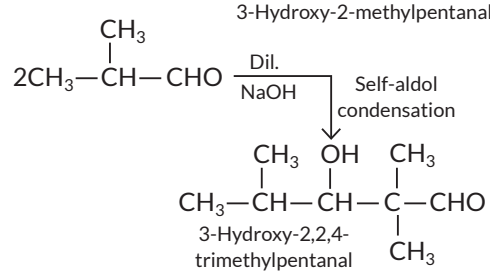
12. $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$
An electronegative group present in the chain withdraws electrons, making O—H bond weaker thus increasing acidity by increasing the ease of releasing H^+. Due to weak $-I$ effect of C_6H_5 group, $C_6H_5CH_2COOH$ is weaker acid than FCH_2COOH and $ClCH_2COOH$. Alcohols are much weaker acids than carboxylic acids as carboxylate ion is resonance stabilised whereas alkoxide ion is not.

13. Propanal and 2-methylpropanal both have α-hydrogen atom, thus, these undergo cross-aldol condensation reaction in presence of dil. NaOH in which each one of them can act either as an electrophile or a nucleophile. Thus,

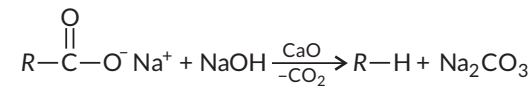
(i) 

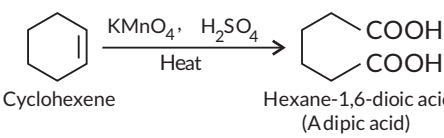
(ii) 

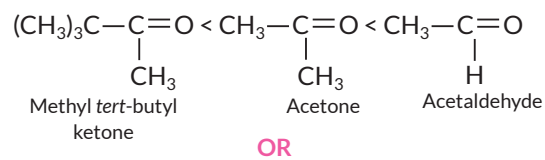
(iii) 

(iv) 

14. Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products. The reaction is termed as decarboxylation reaction.



15. 

16. 

OR

Butan-1-ol has higher boiling point because it undergoes intermolecular hydrogen bonding while butanal has lower boiling point due to absence of hydrogen bonding.

17. (i) The overall acid strength increases in the order.
4-Methoxybenzoic acid < benzoic acid < 4-dinitrobenzoic acid.
(ii) We know that $+I$-effect decreases while $-I$-effect increases the acid strength of carboxylic acids. The overall acid strength increases in the order :

$(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH <$
$CH_3CH_2CH(Br)COOH.$

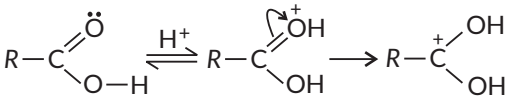
18. Carboxylic acids react with alcohols or phenols in the presence of a mineral acid like concentrated H_2SO_4 or HCl gas as catalyst and give ester. This reaction is called as esterification reaction.

$R-COOH + R'OH \rightleftharpoons R-COOR' + H_2O$

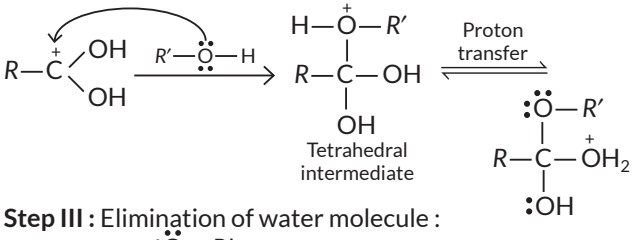
e.g., $CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$
Ethanoic acid Ethanol Ethyl ethanoate

Mechanism of esterification : It is a nucleophilic acyl substitution.

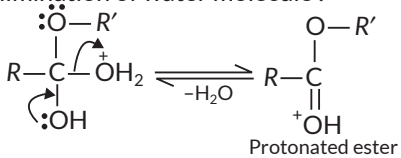
Step I : Protonation of carboxyl oxygen :



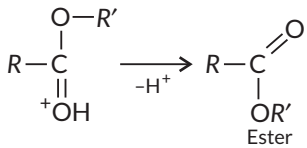
Step II : Nucleophilic addition of alcohol :



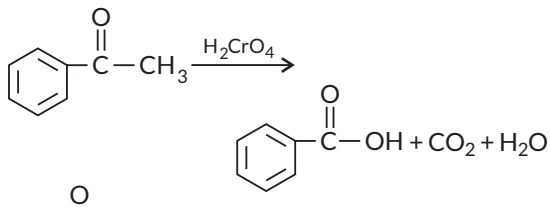
Step III : Elimination of water molecule :



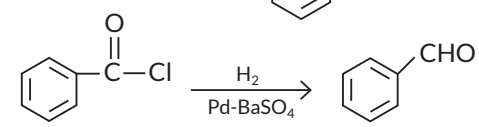
Step IV : Protonated ester loses a proton to give ester :



19. (i)



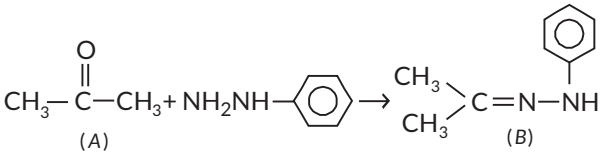
(ii)

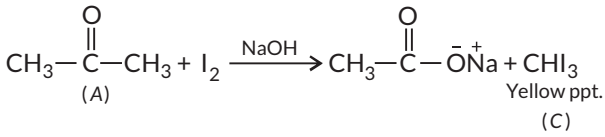


20. Since, compound 'A' (C_3H_6O)reacts with phenylhydrazine. So, it must be either aldehyde or ketone.

As compound 'A' reacts with I_2 in alkaline medium so, it must contains CH_3CO–group so, compound 'A' is ketone

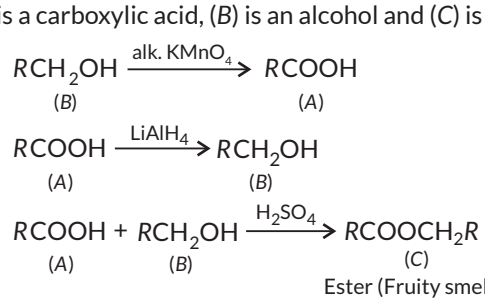
and its structure is $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$



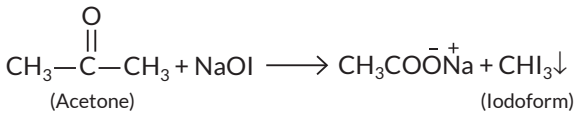


OR

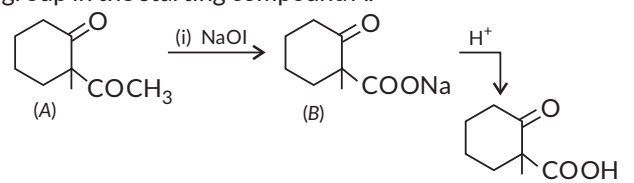
(*A*) is a carboxylic acid, (*B*) is an alcohol and (*C*) is an ester.



21. (i) Iodoform reaction of acetone occurs in following steps :

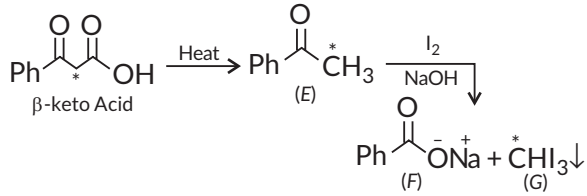


(ii) Given reagents indicate the presence of $-COCH_3$ group in the starting compound *A*.



(iii) Since compound $P(C_3H_6O)$ undergoes iodoform test, it must be CH_3COCH_3 *i.e.*, propan-2-one.

(iv)



OR

Iodoform test is given by the organic compounds having

$CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3-\overset{OH}{\overset{|}{CH}}-$ group.

$CH_3-\underset{CH_3}{\overset{|}{CH}}-OH$: *Iso*-propyl alcohol

CH_3CH_2CHO : Propionaldehyde

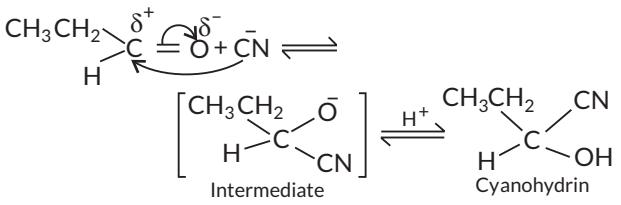
Therefore, *iso*-propyl alcohol will give positive iodoform test.

22. C_3H_6O will have following isomers

(I) CH_3CH_2CHO (II) CH_3COCH_3

Compound (I) will react faster with HCN due to less steric hindrance and greater positive charge on carbon atom of carbonyl group. Two methyl groups increase electron density on carbonyl carbon in compounds (II) hence the rate of nucleophilic attack is less.

Mechanism : $HCN + OH^- \rightarrow CN^- + H_2O$



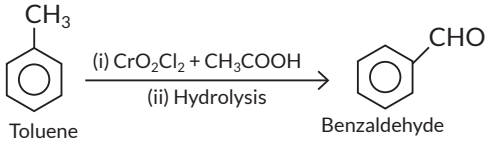
The reaction will not lead to completion since it is a reversible reaction, hence equilibrium is estabilshed.
If a strong acid is added to reaction mixture the addition is inhibited because the formation of CN^- ions from HCN is prevented.

23. $CH_3COOH + CH_3OH \xrightarrow{conc.\ H_2SO_4} CH_3COOCH_3 + H_2O$
Acetic acid (A) | Methyl alcohol | Methyl acetate (B)

$CH_3OH \xrightarrow{mild\ [O]} HCHO \xrightarrow[(ii)\ HCl]{(i)\ 50\%\ KOH} CH_3OH + HCOOH$
Methyl alcohol (A) | Formaldehyde (C) | Methanol (A) | Methanoic acid (D)

$HCOOH \xrightarrow{PCl_5} HCOCl \xrightarrow[\Delta]{NH_3} HCONH_2$
Formic acid (D) | Formyl chloride (E) | Methanamide

Therefore, (A) : Methyl alcohol
(B) : Methyl acetate
(C) : Formaldehyde
(D) : Formic acid or Methanoic acid
(E) : Formyl chloride

24. (a) (i) 

(ii) $R-CHO \xrightarrow[HCl\ gas]{R'OH} R-CH(OR')(OH) \xrightarrow[H^+]{R'OH} R-CH(OR')_2 + H_2O$
Acetal

(b) $CH{\equiv}CH \xrightarrow[H_2SO_4 + HgSO_4]{H_2O} CH_3CHO \xrightarrow{[O]} CH_3COOH$
(Acetylene) | (Acetic acid)

(c) (i) $CH_3-COOH \xrightarrow{PCl_5} CH_3-COCl \xrightarrow[Pd\text{-}BaSO_4]{H_2} CH_3CHO$
(Acetaldehyde)

(ii) $2CH_3-COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\Delta} CH_3-CO-CH_3$
(Acetone)

25. (a) $CH_3CH(Br)CH(CH_3)CH_2CH_3 \xrightarrow[\Delta]{alc.\ KOH} CH_3-CH=C(CH_3)-CH_2CH_3$ (A)

$\xrightarrow[(Markownikoff\ addition)]{HBr} CH_3-CH_2-C(Br)(CH_3)-CH_2CH_3$ (B)

$\xrightarrow{Mg/dry\ ether} CH_3CH_2-C(COOH)(CH_3)-CH_2CH_3 \xleftarrow[2.\ H_3O^+]{1.\ CO_2} CH_3CH_2-C(MgBr)(CH_3)-CH_2CH_3$
(D) | (C)

(b) $CH_3CH_2COOH \xrightarrow[H^+]{C_2H_5OH} CH_3CH_2COOC_2H_5$ (A)

$\xrightarrow[(ii)\ H_2O]{(i)\ 2C_6H_5MgBr} H_3CCH_2-C(C_6H_5)_2-OH$ (B)

$\xrightarrow{\Delta,\ -H_2O} CH_3CH=C(C_6H_5)_2 \xrightarrow{CrO_3,\ \Delta} CH_3COOH + C_6H_5COC_6H_5$
(C) | (D)

OR

Compound *B* gives positive Fehling's test. It shows that it is an aldehyde and gives iodoform test which shows it has —$COCH_3$ group. Compound *C* is a ketone because it does not give Fehling's test but gives iodoform test which shows it also has –$COCH_3$ group.
Hence compound *A* is

$CH_3CH=C(CH_3)-CH_3$

$CH_3CH=C(CH_3)-CH_3 \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} H_3C-CHO + O=C(CH_3)-CH_3$
(A) | (B) | (C)

$CH_3CHO + 3I_2 + 4NaOH \xrightarrow{\Delta}$
(B)

$CHI_3 + HCOO^-Na^+ + 3NaI + 3H_2O$

$CH_3COCH_3 + 3I_2 + 4NaOH \xrightarrow{\Delta}$
(C)

$CHI_3 + CH_3COO^-Na^+ + 3NaI + 3H_2O$

CHAPTER

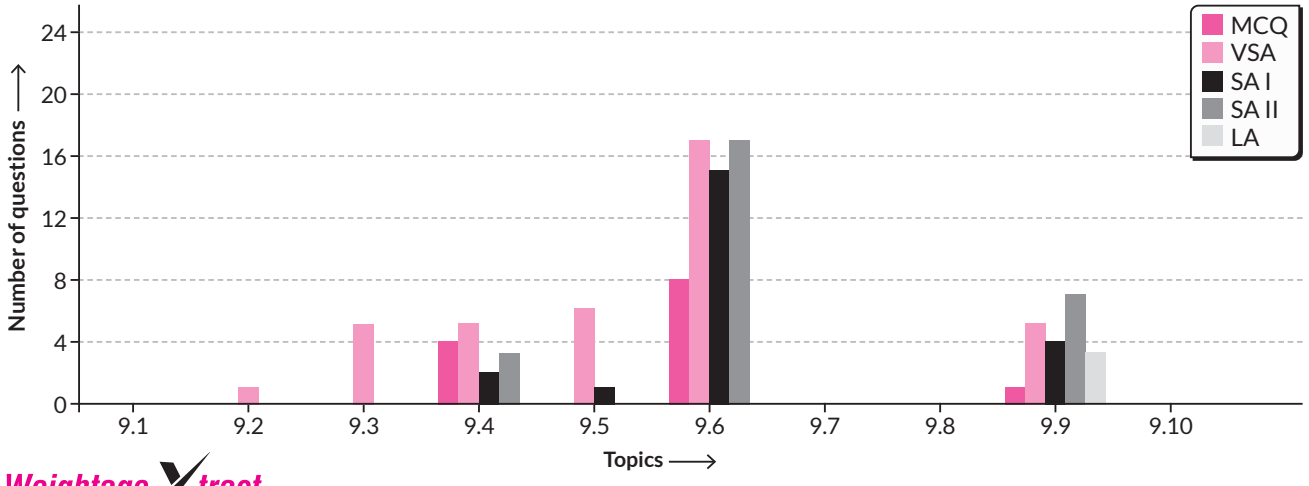
9

Amines

TOPICS

9.1 Structure of Amines
9.2 Classification
9.3 Nomenclature
9.4 Preparation of Amines
9.5 Physical Properties
9.6 Chemical Reactions
9.7 Method of Preparation of Diazonium Salts
9.8 Physical Properties
9.9 Chemical Reactions
9.10 Importance of Diazonium Salts in Synthesis of Aromatic Compounds

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



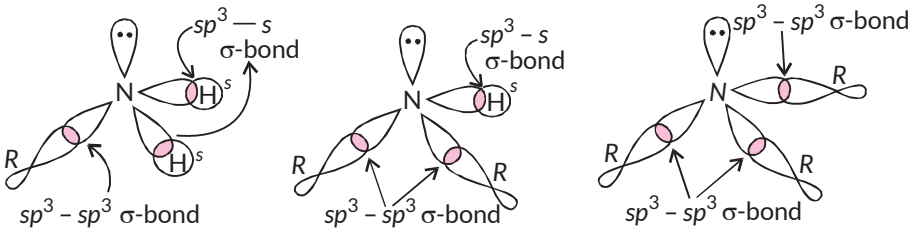
Weightage Xtract

- Topic 9.6 is highly scoring topic.
- Maximum total weightage is of Topic 9.6 *Chemical Reactions*.
- Maximum MCQ, VSA, SA I, SA II type questions were asked from Topic 9.6 *Chemical Reactions*.

QUICK RECAP

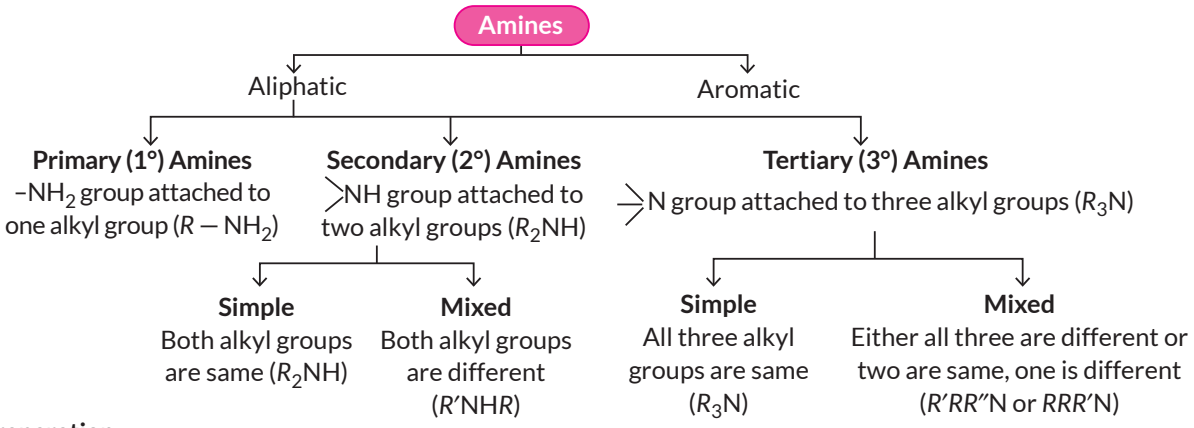
AMINES

- **Amines :** These are alkyl or aryl derivatives of ammonia and are obtained by replacing one, two or three hydrogen atoms by alkyl/aryl groups.
- **Nomenclature :** In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, *alkylamine*. In IUPAC system, amines are named as *alkanamines*. In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is added before the name of alkyl group.
- **Structure :** Nitrogen orbitals in amines are sp^3-hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle C — N — *E*, (where *E* is C or H) is less than 109.5°.

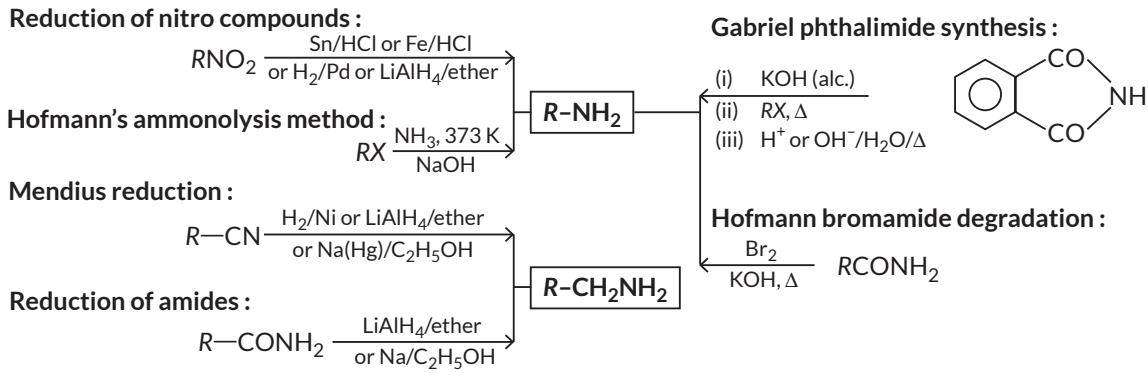


Orbital structure of 1°, 2° and 3° amines

Classification :


Amines
Aliphatic
Aromatic
Primary (1°) Amines
–NH2 group attached to one alkyl group (R — NH2)
Secondary (2°) Amines
>NH group attached to two alkyl groups (R2NH)
Tertiary (3°) Amines
>N group attached to three alkyl groups (R3N)
Simple
Both alkyl groups are same (R2NH)
Mixed
Both alkyl groups are different (R′NHR)
Simple
All three alkyl groups are same (R3N)
Mixed
Either all three are different or two are same, one is different (R′RR″N or RRR′N)

Preparation :



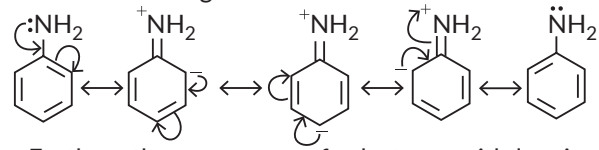
- **Limitations of Gabriel phthalimide synthesis :**
  - It is used for the preparation of only 1° amines. *tert*-Butylamine is a 1° amine, but cannot be prepared by this method. In this case, elimination takes place.
  - Aromatic 1° amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

Physical properties :

- Lower amines are gases and liquids but higher amines are solids.
- Primary and secondary amines have higher boiling points than alcohols and alkanes of almost the same molar mass due to hydrogen bonding.
  Order of boiling points of isomeric amines: 1° > 2° > 3°
- Primary and secondary amines are soluble in water due to hydrogen bonding between —NH_2 and H_2O molecules.

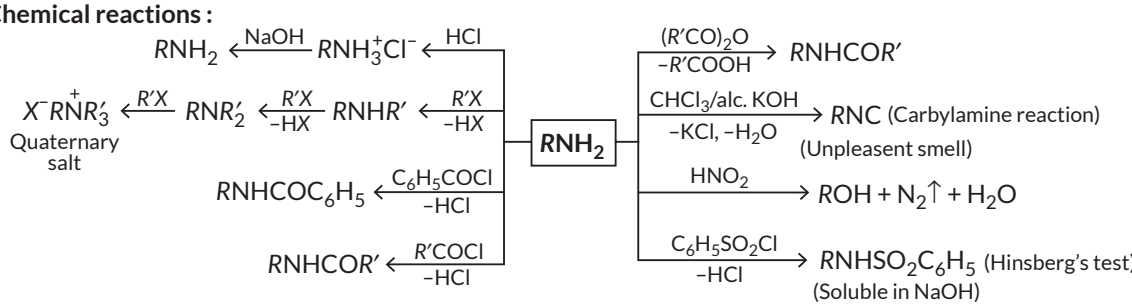
Chemical properties :

- **Basic character of amines :**
  - Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom. Larger the value of K_b or smaller the value of pK_b, stronger is the base.
  - Aliphatic amines are stronger bases than ammonia due to *+I* effect of alkyl groups present in amines.
  - Aromatic amines are weaker bases than ammonia due to *–I* effect of aryl group.
  - Beside inductive effect, there are other effects like steric effect, solvation effect, resonance effect which affect the basic strength of amines.
  - In gaseous phase, the order of basicity of amines is 3° amine > 2° amine > 1° amine > NH_3.
  - In aqueous phase, despite inductive effect, solvation effect and steric hindrance also play important roles. Thus, the order of basicity of amines is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ and $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
  - Aniline is a weaker base compared to ammonia. This is because the lone pair of electrons on N-atom of aniline is less available for protonation due to its involvement in conjugation with the π-electrons of the benzene ring.



Further the presence of electron withdrawing groups like —NO_2, —CN, —*X*, etc., decreases the basicity while, the presence of electron donating groups like —OCH_3, —CH_3, —NH_2, etc., activates the benzene ring and also increases the basicity.

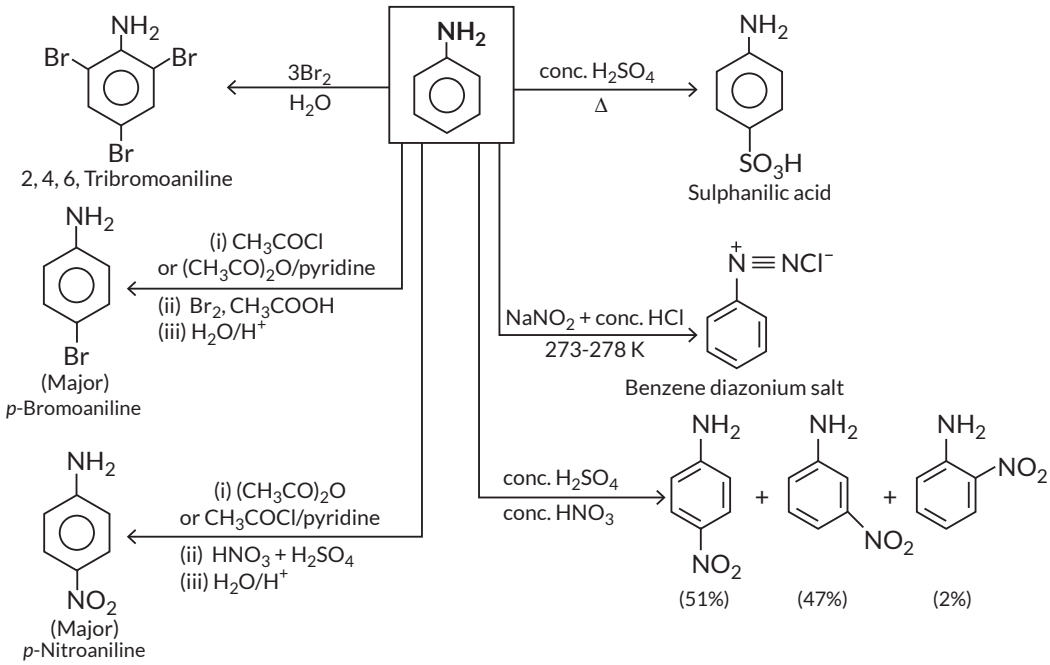
▶ **Chemical reactions :**


RNH2
RNH2 ← NaOH RNH3+Cl− ← HCl
X−RNR'3 ← R'X RNR'2 ← R'X, −HX RNHR' ← R'X, −HX
Quaternary salt
RNHCOC6H5 ← C6H5COCl, −HCl
RNHCOR' ← R'COCl, −HCl
(R'CO)2O, −R'COOH → RNHCOR'
CHCl3/alc. KOH, −KCl, −H2O → RNC (Carbylamine reaction)
(Unpleasent smell)
HNO2 → ROH + N2↑ + H2O
C6H5SO2Cl, −HCl → RNHSO2C6H5 (Hinsberg's test)
(Soluble in NaOH)

▶ **Identification of primary, secondary and tertiary amines :**

Test	Primary amine	Secondary amine	Tertiary amine
Reaction with nitrous acid	Gives alcohol with effervescence of N_2 gas.	Gives oily nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold which is soluble in water and on heating gives nitrosoamine.
Reaction with benzene sulphonyl chloride (*Hinsberg's reagent*)	Gives *N*-alkylbenzene-sulphonamide which is soluble in alkali.	Gives *N*,*N*-dialkylbenzene sulphonamide which is insoluble in alkali.	No reaction
Carbylamine test : Reaction with chloroform and alcoholic KOH	Forms carbylamine or isocyanide (*R*NC) with characteristic unpleasant odour.	No reaction	No reaction

▶ **Electrophilic substitution reactions of arylamines :** Aniline undergoes electrophilic substitution reactions. $—NH_2$ group is *ortho*- and *para*-directing and a powerful activating group.



DIAZONIUM SALTS

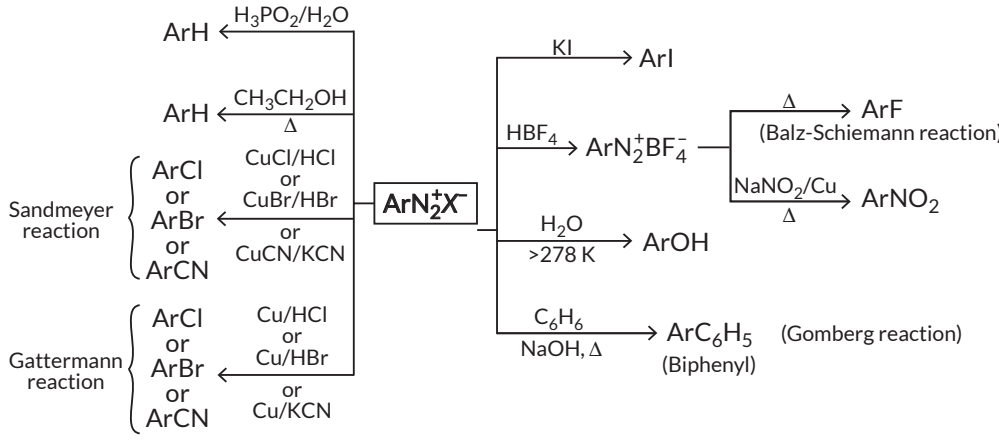
- **Arenediazonium salts :** They have the general formula $ArN_2^+X^-$, Ar stands for the aryl ($—C_6H_5$) group and X^- is Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^- etc.
- **Nomenclature :** They are named by suffixing diazonium to the name of parent hydrocarbon followed by anion.
- **Preparation :** Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid (sodium nitrite and hydrochloric acid) at 0-5 °C.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5°C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

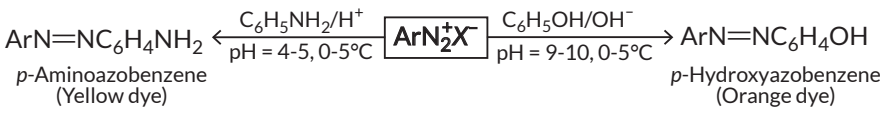
- **Stability :** Arenediazonium salts are more stable (for short time) than alkanediazonium salts due to dispersal of positive charge over the benzene ring.
- **Physical properties :** These are generally colourless, crystalline solids, which are soluble in water. They are unstable and explode in dry state.

Chemical properties :

Reactions involving displacement of nitrogen (diazo group) :



Reactions involving retention of diazo group (coupling reactions) :



ORGANIC COMPOUNDS CONTAINING NITROGEN

Amines

N → sp^3, classified as 1°, 2°, 3° depending upon the no. of H atoms replaced by alkyl or aryl groups in NH_3. IUPAC name : alkanamines or arylamines.

Preparation

- $R-COOH + NH_3 \xrightarrow[\text{Schmidt reaction}]{\text{Conc. } H_2SO_4}$
- $R-CN \xrightarrow[\text{Mendius reaction}]{H_2/Ni;\ Na/C_2H_5OH}$
- $R-NO_2 \xrightarrow{Sn/HCl;\ LiAlH_4}$

$\boxed{R-NH_2}$

- $\xrightarrow[H_2O;\ HCl,\ \Delta]{KOH;\ RX}$

Gabriel phthalimide synthesis

Chemical Properties

$RNH_2 \xrightarrow[\text{Carbylamine reaction}]{CHCl_3 + 3KOH,\ \Delta}$ *R*NC (Alkyl isocyanide)

$RNH_2 \xrightarrow[\Delta]{R'-CHO}$ $RN=CHR'$ (Schiff's base (Aldimine))

Separation of 1°, 2° and 3° amines

Hofmann's method

Diethyloxalate + 1° + 2° + 3° amines

- Oxamide, solid (1° amine)
- Oxamic ester, liquid (2° amine)
- No reaction (3° amine)

Aniline

Preparation

- $C_6H_5NO_2 \xrightarrow[\text{or, Fe/HCl}]{Sn/HCl}$
- $C_6H_5COOH + N_3H \xrightarrow[\text{Schmidt reaction}]{\text{Conc. } H_2SO_4}$
- $C_6H_5OH + NH_3 \xrightarrow[300\ °C]{\text{Anhy. } ZnCl_2}$

$\boxed{C_6H_5NH_2}$

Preparation

$C_6H_5NH_2 \xrightarrow{HCl/0\text{-}5\ °C} C_6H_5NH_3^+Cl^-$

$\xrightarrow{[O]/\text{acidified } KMnO_4}$ Aniline black

$\xrightarrow{[O]/\text{alkaline } KMnO_4}$ Azobenzene

$\xrightarrow{[O]/\text{neutral } KMnO_4}$ Azobenzene and nitrobenzene

Preparation

- $RX + AgCN \xrightarrow[\Delta]{C_2H_5OH}$
- $RNHCHO \xrightarrow[\text{Pyridine}]{POCl_3}$

$\boxed{RNC}$

Isocyanides

Chemical Properties

$\boxed{RNC} \xrightarrow{H_2O/H^+} RNH_2$

$\xrightarrow[Na/C_2H_5OH]{+4[H]} RNHCH_3$

$\xrightarrow[250°C]{\Delta} RCN$

Chemical Properties

$\boxed{RCN} \xrightarrow[SnCl_2/HCl]{+2[H]} RCHO$ (Stephen's reaction)

$\xrightarrow[\text{alk. } H_2O_2]{R'MgX,\ H_2O} RCOR'$ / $RCOOH$

Diazonium Salts

Preparation

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0\text{-}5°C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

Chemical Properties

$\boxed{C_6H_5N_2^+Cl^-}$

$\xrightarrow[\Delta]{CuCl/HCl} C_6H_5Cl$ [Sandmeyer reaction]

$\xrightarrow{Cu/HCl} C_6H_5Cl$ [Gattermann reaction]

$\xrightarrow[NaOH,\ \Delta]{C_6H_6} C_6H_5-C_6H_5$ [Gomberg reaction]

$\xrightarrow{Phenol} C_6H_5N=NC_6H_4OH$ [Coupling reaction]

$\xrightarrow{H_2O/H^+} C_6H_5OH$

$\xrightarrow{HBF_4/\Delta} C_6H_5F$

Cyanides

Preparation

- $RX + KCN \xrightarrow[\Delta]{100\ °C}$
- $R-CONH_2 \xrightarrow[\Delta]{P_2O_5}$

$\boxed{RCN}$

BRAIN MAP

Previous Years' CBSE Board Questions

9.2 Classification

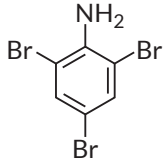
VSA (1 mark)

1. Choose the primary amine from the following compounds :
$(C_2H_5)_2CHNH_2$, $(C_2H_5)_2NH$, $(CH_3)_3N$
(Term II, 2021-22C) U

9.3 Nomenclature

VSA (1 mark)

2. Write IUPAC name of the following compound :
$(CH_3CH_2)_2NCH_3$ *(Delhi 2017)* U
3. Write the structure of 2, 4-dinitrochlorobenzene.
(Delhi 2017)
4. Write the IUPAC name of the following compound :
$CH_3NHCH(CH_3)_2$ *(Delhi 2017)*
5. Write IUPAC name of the following compound:
$(CH_3)_2N - CH_2CH_3$ *(Delhi 2017)*
6. Write the IUPAC name of the given compound :



(Delhi 2016) U

9.4 Preparation of Amines

MCQ

7. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives
(a) CH_3COONa (b) CH_3NH_2
(c) CH_3CH_2Br (d) $CH_3CH_2NH_2$
(2023)
8. **Assertion :** Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.
Reason : Ammonolysis of alkyl halides yields mainly secondary amines.
(a) Both Assertion (A) and Reason (R) are true and Reason is the correct explanation of the assertion.
(b) Both Assertion (A) and Reason (R) are true, but Reason is not the correct explanation of the assertion.
(c) Assertion (A) is true, but Reason (R) is false.
(d) Assertion (A) is false, but Reason (R) is true.
(2023)
9. Which of the following would not be a good choice for reducing nitrobenzene to aniline?
(a) $LiAlH_4$ (b) H_2/Ni
(c) Fe and HCl (d) Sn and HCl *(2023)*
10. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives
(a) $CH_3CH_2NH_2$ (b) CH_3CH_2Br
(c) CH_3NH_2 (d) CH_3COONa
(2020) U

VSA (1 mark)

11. Ammonolysis of alkyl halides is not a good method to prepare pure primary amines. Give reason
(1/5, 2020) Ap
12. Write the structures of *A* and *B* in the following reaction :
$CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B$ *(1/5, 2020)*
13. Carry out the following conversion :
Benzoic acid to aniline. *(1/5, AI 2019)*
14. Write the chemical equation involved in the following reaction :
Hoffmann bromamide degradation reaction
(AI 2019, 1/5, 2018, 1/2, AI 2016)
15. How do you convert the following :
Ethanenitrile to ethanamine *(1/3, AI 2015)*

SA I (2 marks)

16. Complete the following :
$CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B$ *(Term II, 2021-22C)*
17. How will you convert the following :
(i) Nitrobenzene into aniline
(ii) Ethanoic acid into methanamine
(2/3, Delhi 2014)

SA II (3 marks)

18. (a) Write the IUPAC name for the following organic compound : $(CH_3CH_2)_2NCH_3$
(b) Write the equations for the following :
(i) Gabriel phthalimide synthesis
(ii) Hoffmann bromamide degradation
(Term II, 2021-22) R
19. An aromatic compound '*A*' ($C_7H_6O_2$) on reaction with aqueous ammonia and heating forms compound '*B*'. '*B*' on heating with Br_2 and alcoholic potash forms a compound '*C*' of molecular formula C_6H_7N. Write the reactions involved and identify '*A*', '*B*', '*C*'.
(Term II, 2021-22)

OR

An aromatic compound '*A*' on treatment with aqueous ammonia and heating forms compound '*B*' which on heating with Br_2 and KOH forms a compound '*C*' of molecular formula C_6H_7N. Write

the structures and IUPAC names of compounds *A*, *B* and *C*. *(Delhi 2015C)*

20. How will you carry out the following conversions :
(i) Nitrobenzene to aniline
(ii) Ethanamide to methanamine
(iii) Ethanenitrile to ethanamine
(Term II, 2021-22) Ap

9.5 Physical Properties

VSA (1 mark)

21. Out of CH_3NH_2 and CH_3OH, which has higher boiling point? *(2020)*

22. Arrange the following compounds in decreasing order of their boiling points :
Butanol, Butanamine, Butane *(1/3, 2020)* Ev

23. Propanamine and *N*,*N*-dimethylmethanamine contain the same number of carbon atoms, even though propanamine has higher boiling point than *N*,*N*-dimethylmethanamine. Why? *(AI 2019)*
OR
Give reasons for the following :
Primary amines have higher boiling point than tertiary amines. *(1/3, AI 2016, 2014)*
OR
Out of CH_3NH_2 and $(CH_3)_3N$, which one has higher boiling point? *(Delhi 2014C)*

24. Arrange the following in the increasing order of their boiling points :
$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$
(2019, 1/5, Delhi 2015)

25. Arrange the following compounds in increasing order of solubility in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$
(Delhi 2014) Cr

26. Account for the following :
Ethylamine is soluble in water whereas aniline is not. *(1/3, Delhi 2014C)* Cr

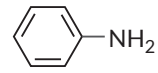
SA I (2 marks)

27. Arrange the following compounds as directed :
(i) In increasing order of solubility in water :
$(CH_3)_2NH$, CH_3NH_2, $C_6H_5NH_2$
(ii) In increasing order of boiling point :
$(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_2H_5NH_2$ *(2/3, 2020)*

9.6 Chemical Reactions (Amines)

Basicity of Amines

MCQ

28. Which of the following is least basic?
(a) $(CH_3)_2NH$ (b) NH_3
(c)  (d) $(CH_3)_3N$ *(2023)*

29. **Assertion (A) :** —NH_2 group is *o*- and *p*-directing in electrophilic substitution reactions.
Reason (R) : Aniline cannot undergo Friedel-Crafts reaction.
(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is true, but Reason (R) is false.
(d) Assertion (A) is false, but Reason (R) is true.
(2023)

30. **Assertion (A) :** Acetylation of aniline gives a monosubstituted product.
Reason (R) : Activating effect of —$NHCOCH_3$ group is more than that of amino group.
(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is true, but Reason (R) is false.
(d) Assertion (A) is false, but Reason (R) is true.
(2023)

31. **Assertion (A) :** $(C_2H_5)_2NH$ is more basic than $(C_2H_5)_3N$ in aqueous solution.
Reason (R) : In $(C_2H_5)_2NH$, there is more steric hindrance and +*I* effect than $(C_2H_5)_3N$.
(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is true, but Reason (R) is false.
(d) Assertion (A) is false, but Reason (R) is true.
(2023)

32. In the reaction
$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow A + 3B + 3C$
The product *A* is
(a) C_6H_5NC (b) C_6H_5CN
(c) C_6H_5Cl (d) $C_6H_5NHCH_3$
(2023)

33. Out of the following, the strongest base in aqueous solution is
(a) methylamine (b) dimethylamine
(c) trimethylamine (d) aniline. *(2020)* An

VSA (1 mark)

34. Arrange the following compounds as directed :
In decreasing order of basic strength in aqueous solution :
$(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2 *(1/3, 2020)* Cr

35. Arrange the following in decreasing order of basic character :
$C_6H_5NH_2$, $(CH_3)_3N$, $C_2H_5NH_2$ *(2019)*

36. Arrange the following in increasing order of base strength in gas phase.
$(C_2H_5)_3N$, $C_2H_5NH_2$, $(C_2H_5)_2NH$ *(Delhi 2019)*

37. Give reason :
$(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. *(1/5, 2018)*

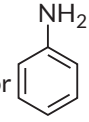
38. Arrange the following in the decreasing order of their basic strength in aqueous solutions :
CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ and NH_3 *(1/3, 2018C)*

39. Arrange the following in increasing order of basic strength :
Aniline, *p*-nitroaniline and *p*-toluidine
(1/2, AI 2015, AI 2015C)

40. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$
(1/2, AI 2015, Delhi 2014)

41. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$ *(Delhi 2014)*

42. Which of the two is more basic and why?



CH_3NH_2 or *(Foreign 2014)* U

SA I (2 marks)

43. Explain briefly
(a) Carbylamine reaction
(b) Gabriel phthalimide synthesis *(2023)*

44. (i) Draw the zwitter ion structure for sulphanilic acid.
(ii) How can the activating effect of $-NH_2$ group in aniline be controlled? *(2023)*

45. Arrange the following compounds as directed: (any two)
(i) In decreasing order of basic strength in aqueous solution :
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$
(ii) In increasing order of solubility in water :
$(C_2H_5)_2NH$, $C_2H_5NH_2$, $C_6H_5NH_2$
(iii) In decreasing order of their pK_b values :
$C_6H_5NH_2$, $C_2H_5NH_2$, NH_3 *(Term II, 2021-22)*

46. (i) Arrange the following compounds in an increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2
(ii) Arrange the following compounds in a decreasing order of pK_b values :
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$ *(Delhi 2014C)*

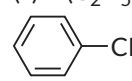
Chemical Properties of Amines

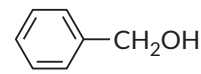
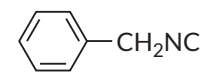
MCQ

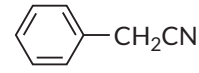
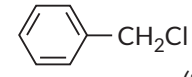
47. Read the passage given below and answer the questions (i to iv) :
Amines can be considered as derivatives of ammonia and are usually formed from nitriles, nitro, halides, amides, etc. They show hydrogen bonding which influences their physical properties. In aromatic amines, electron releasing and withdrawing groups respectively increase and decrease their basic character.
Hinsberg test is used for the identification and distinction between primary, secondary and tertiary amines.
The following questions are multiple choice questions:
(i) Ethyl amine can be prepared by the action of $LiAlH_4$ on
(a) CH_3NO_2 (b) $CH_3—CN$
(c) $CH_3—NC$ (d) $CH_3—CH_2—CONH_2$
(ii) Which of the following reagents is used for the Hinsberg test of amines ?
(a) C_6H_5COCl (b) CH_3COCl
(c) $C_6H_5—SO_3H$ (d) $C_6H_5—SO_2Cl$
(iii) Out of the following, the strongest base in aqueous solution is
(a) $(CH_3)_2NH$ (b) $(CH_3)_3N$
(c) $CH_3—NH_2$ (d) $C_6H_5—NH_2$
(iv) The reaction of ammonia with a large excess of $CH_3—Cl$ will give mainly
(a) C_2H_6 (b) $(CH_3)_2NH$
(c) $(CH_3)_4N^+Cl^-$ (d) $CH_3—NH_2$

OR

Among the following amines, which one is expected to have the lowest boiling point?
(a) $C_2H_5—NH_2$ (b) $(C_2H_5)_3N$
(c) $(C_2H_5)_2NH$ (d) $CH_3—NH_2$ *(2021C)*

48.  on heating with $CHCl_3$ and alcoholic KOH gives foul smell of

(a)  (b) 

(c)  (d) 

(2020)

VSA (1 mark)

49. Write an isomer of C_3H_9N which gives foul smell of isocyanide when treated with chloroform and ethanolic NaOH. *(2020)*

50. Give the structures of *A* and *B* in the following sequence of reactions :

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[0-5°C]{NaNO_2+HCl} B$$ *(2/3, 2020)*

51. Carry out the following conversion :
Bromomethane to ethanol. *(1/5, AI 2019)* Cr

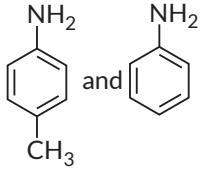
52. Describe the following by giving the relevant chemical equation :
Carbylamine reaction *(1/3, 2018C)* R

53. Give a simple chemical test to distinguish between the following pair of compounds :
$(CH_3)_2NH$ and $(CH_3)_3N$ *(1/5, Delhi 2015)*

54. How will you convert the following :
Aniline into *N*-phenylethanamide
(Write the chemical equations involved.)
(1/3, Delhi 2014)

55. Which of the two is more basic and why?
CH_3NH_2 or NH_3 *(Foreign 2014)* U

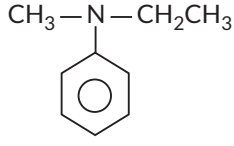
56. Which of the two is more basic and why?



(Foreign 2014) U

SA I (2 marks)

57. (a) Write the IUPAC name for the following organic compounds:



(b) Complete the following:

$$C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{Br_2/H_2O} B$$ *(2023)*

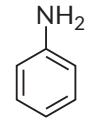
58. How will you distinguish between the following pairs of compounds :
(i) Aniline and ethanamine
(ii) Aniline and *N*-methylaniline *(2/3, 2020)* Cr

59. Distinguish between the following :
(i) $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$
(ii) Aniline and CH_3NH_2 *(2/5, 2020)*

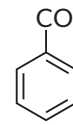
60. Give reasons :
(i) Although $-NH_2$ group is *o/p* directing in electrophilic substitution reactions, yet aniline, on nitration gives good yield of *m*-nitroaniline.
(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. *(2/5, 2020)*

61. Account for the following :
(a) Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.
(b) On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali. *(2019)* U

62. Write structures of compounds *A* and *B* in each of the following reactions :

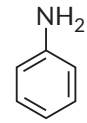
(a) 

$\xrightarrow{conc.\ H_2SO_4} A \xrightarrow{Heat,453-473K} B$

(b) 

$\xrightarrow{Br_2/NaOH} A \xrightarrow{(CH_3CO)_2O/pyridine} B$
(2019 C)

63. Write the structures of the main products of the following reactions :

(i) 

$\xrightarrow[Pyridine]{(CH_3CO)_2O}$

(ii)

$\xrightarrow{(CH_3)_2NH}$ *(2/5, 2018)* An

64. (a) Give a simple chemical test to distinguish between aniline and *N*, *N*-dimethylaniline.
(b) Arrange the following in the increasing order of their pK_b values :
$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$ *(2/5, 2018)*

65. Give reasons for the following :
(i) Aniline does not undergo Friedel–Crafts reaction.
(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. *(2/3, AI 2016, 2014)*

66. Illustrate the following reactions giving suitable example in each case :
(i) Ammonolysis
(ii) Acetylation of amines *(2/5, Foreign 2015)*

67. Account for the following :
(i) Aniline does not give Friedel–Crafts reaction.
(ii) pK_b of methylamine is less than that of aniline.
(2/3, Delhi 2014C) U

SA II (3 marks)

68. Illustrate the following reactions giving suitable example in each case:
(i) Gabriel phthalimide synthesis.
(ii) Carbylamine reaction.
(iii) Hoffmann bromamide degradation reaction.
(Term II, 2021-22)

69. Give reasons :
(i) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

(ii) Aniline does not give Friedel-Crafts reaction.
(iii) Although $-NH_2$ group is *o/p* directing in electrophilic substitution reactions, yet aniline on nitration gives good yield of *m*-nitroaniline.
(Term II, 2021-22) Ap

70. Write equations involved in the following reactions :
(i) Ethanamine reacts with acetyl chloride.
(ii) Aniline reacts with bromine water at room temperature.
(iii) Aniline reacts with chloroform and ethanolic potassium hydroxide. *(Term II, 2021-22)*

71. Account for the following :
(i) pK_b of aniline is more than that of methylamine.
(ii) Aniline does not undergo Friedel-Crafts reaction.
(iii) Primary amines have higher boiling points than tertiary amines. *(Term II, 2021-22)* Ap

72. (i) Arrange the following compounds in the increasing order of their basic strength in aqueous solution : CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$
(ii) What is Hinsberg's reagent ?
(iii) What is the role of pyridine in the acylation reaction of amines ? *(Term II, 2021-22)*

73. A compound '*A*' on reduction with iron scrap and hydrochloric acid gives compound '*B*' with molecular formula C_6H_7N. Compound '*B*' on reaction with $CHCl_3$ and alcoholic KOH produces an obnoxious smell of carbylamine due to the formation of '*C*'. Identify '*A*', '*B*' and '*C*' and write the chemical reactions involved. *(Term II, 2021-22)* Cr

74. Write reasons for the following :
(i) Ethylamine is soluble in water whereas aniline is insoluble.
(ii) Amino group is *o*- and *p*-directing in aromatic electrophilic substitution reactions, but aniline on nitration gives a substantial amount of *m*-nitroaniline.
(iii) Amines behave as nucleophiles.
(Term II, 2021-22)

75. An organic compound (*A*) with molecular formula C_3H_7NO on heating with Br_2 and KOH forms a compound (*B*). Compound (*B*) on heating with $CHCl_3$ and alcoholic KOH produces a foul smelling compound (*C*) and on reacting with $C_6H_5SO_2Cl$ forms a compound (*D*) which is soluble in alkali. Write the structures of (*A*), (*B*), (*C*) and (*D*).
(Term II, 2021-22) Cr

76. Account for the following :
(a) Aniline is a weaker base compared to ethanamine.
(b) Aniline does not undergo Friedel-Crafts reaction.
(c) Only aliphatic primary amines can be prepared by Gabriel Phthalimide synthesis. *(2020)*

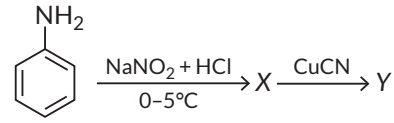
77. (a) Write the chemical reaction of methyl amine with benzoyl chloride and write the IUPAC name of the product obtained.
(b) Arrange the following in the increasing order of their pK_b values :
$C_6H_5NH_2$, NH_3, $C_2H_5NH_2$, $(C_2H_5)_2NH$ *(3/5, 2020)*

78. Give reasons :
(i) Aniline does not undergo Friedel-Crafts' reaction.
(ii) Aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis.
(iii) Aliphatic amines are stronger bases than ammonia. *(2020)* U

79. Describe a method for the identification of $C_2H_5NH_2$, $(C_2H_5)_2NH$ and $(C_2H_5)_3N$. Also write the chemical equations for the reactions involved.
(2020C)

80. (a) Give one chemical test to distinguish between the compounds of the following pairs :
(i) CH_3NH_2 and $(CH_3)_2NH$
(ii) Aniline and ethanamine
(b) Why aniline does not undergo Friedel–Crafts reaction? *(AI 2019)* Cr

81. (a) Identify *X* and *Y* in the following :



(b) Amino group is *o*, *p*-directing for aromatic electrophilic substitution reactions. Why does aniline on nitration give *m*-nitroaniline?
(2019C)

82. Give reasons :
(i) Acetylation of aniline reduces its activation effect.
(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.
(iii) Although $-NH_2$ is *o/p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline. *(Delhi 2017)*

83. Write the structures of main products when aniline reacts with the following reagents :
(i) Br_2 water (ii) HCl
(iii) $(CH_3CO)_2O$/pyridine *(3/5, Delhi 2015)*

84. Give the structures of products *A*, *B* and *C* in the following reactions :

(i) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow[alc.\ NaOH]{CHCl_3 +} C$

(Delhi 2014) An

9.9 Chemical Reactions (Diazonium salts)

MCQ

85. In cold conditions, aniline is diazotized and then treated with aniline again to give a coloured product. The structure of the coloured product is

(a) $(CH_3)_2$—N—⬡—NH—⬡

(b) H_2N—⬡—N=N—⬡

(c) H_2N—⬡—NH—⬡

(d) HO—⬡—N=N—⬡ *(2020C)*

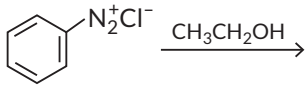
VSA (1 mark)

86. Write the structures of *A* and *B* in the following reactions :

$C_6H_6N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B$ *(1/5, 2020)* Ev

87. Carry out the following conversion :
p-nitrotoluene to 2-bromobenzoic acid.
(1/5, AI 2019)

88. Write the structure of the main product of the following reaction :



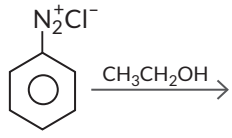
(1/5, 2018) Ap

89. Complete the following reaction equation :
$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$
(Delhi 2015C)

90. The conversion of primary aromatic amines into diazonium salts is known as _____. *(AI 2014)*

SA I (2 marks)

91. (i) Complete the reaction with the main product formed:



(ii) Convert bromoethane to propanamine. *(2023)*

92. (a) Write the reaction involved in the following :
Diazotisation

(b) Give reason :
Aromatic diazonium salts are more stable than aliphatic diazonium salts. *(2/5, 2018)* Ap

93. How do you convert the following :
(i) $C_6H_5CONH_2$ to $C_6H_5NH_2$
(ii) Aniline to phenol *(2/3, AI 2015)* Ev

94. Give the structures of *A*, *B* and *C* in the following reactions :

(i) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{H_2O} C$

(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2 + KOH} C$

(2/3, Delhi, AI 2014) An

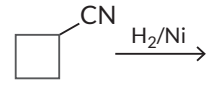
SA II (3 marks)

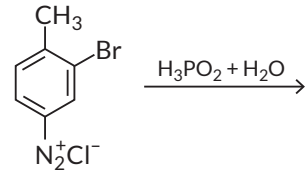
95. (a) Illustrate Sandmeyer's reaction with an equation.

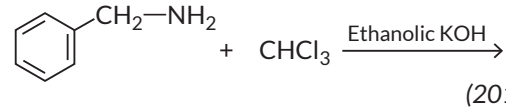
(b) Explain why $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in aqueous solution. *(2023)*

96. Write the structures of main products when benzene diazonium chloride reacts with the following reagents :
(i) CuCN (ii) CH_3CH_2OH
(iii) KI *(Delhi 2019)* An

97. Complete the following reactions :

(a) 

(b) 

(c) 

(2019)

98. How do you convert the following :
(a) *N*-phenylethanamide to *p*-bromoaniline
(b) Benzenediazonium chloride to nitrobenzene
(c) Benzoic acid to aniline *(2019)*

99. Write the structures of compounds *A*, *B* and *C* in the following reactions :

(a) $CH_3—COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH_{(aq)}} B \xrightarrow{CHCl_3 + alc.\ KOH} C$

(b) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/pyridine} C$

(AI 2017)

100. Write the structures of *A*, *B* and *C* in the following :

(i) $C_6H_5—CONH_2 \xrightarrow{Br_2/aq.\ KOH} A \xrightarrow[0\text{-}5°C]{NaNO_2 + HCl} B \xrightarrow{KI} C$

(ii) $CH_3—Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[\Delta]{CHCl_3 + alc.\ KOH} C$

(Delhi 2016) Cr

101. Write the structures of *A*, *B* and *C* in the following reactions :

(i) $C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O} C$

(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(3/5, Foreign 2015) Ev

LA (5 marks)

102. Read the following passage and answer the questions that follow :

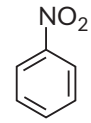
Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl groups. Amines are usually formed from nitro compounds, halides, amides, etc. They exhibit hydrogen bonding which influences their physical properties. Alkyl amines are found to be stronger bases than ammonia. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Reactivity of aromatic amines can be controlled by acylation process.

(i) Why does aniline not give Friedel-Crafts reaction ?

(ii) Arrange the following in the increasing order of their pK_b values :
$C_6H_5NH_2$, NH_3, $C_2H_5NH_2$, $(CH_3)_3N$

(iii) How can you distinguish between $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$ by Hinsberg test ?

(iv) (a) Write the structures of *A* and *B* in the following reactions :

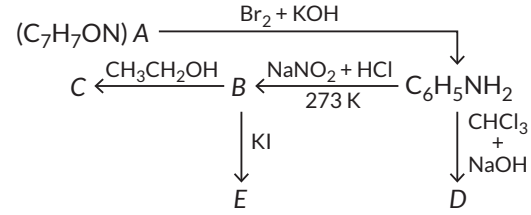
(I) 

(II) $CH_3CH_2CONH_2 \xrightarrow{Br_2/alc.\ KOH} A \xrightarrow[Pyridine]{CH_3COCl} B$

OR

(b) How will you convert the following
(I) Benzoic acid to aniline
(II) Aniline to *p*-bromoaniline *(Term-II, 2021-22)*

103. An aromatic compound '*A*' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions :



(Delhi 2015) Cr

104. (i) Write the structures of main products when benzenediazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents :
(a) HBF_4/Δ (b) Cu/HBr

(ii) Write the structures of *A*, *B* and *C* in the following reactions :

(a) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O} C$

(b) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$

(Foreign 2015) U

CBSE Sample Questions

9.4 Preparation of Amines

MCQ

1. Propanamide on reaction with bromine in aqueous NaOH gives
(a) propanamine (b) ethanamine
(c) *N*-methylethanamine (d) propanenitrile.
(2020-21)

9.5 Physical Properties

MCQ

2. Arrange the following in the increasing order of their boiling points:
A : Butanamine, *B* : *N*,*N*-Dimethylethanamine, *C* : *N*-Ethylethanamine
(a) *C* < *B* < *A* (b) *A* < *B* < *C*
(c) *A* < *C* < *B* (d) *B* < *C* < *A*
(2022-23) Ap

9.6 Chemical Reactions (Amines)

MCQ

3. Which of the following statements is not correct for amines?
(a) Most alkyl amines are more basic than ammonia solution.
(b) pK_b value of ethylamine is lower than benzylamine.
(c) CH_3NH_2 on reaction with nitrous acid releases NO_2 gas.
(d) Hinsberg's reagent reacts with secondary amines to form sulphonamides. *(2022-23)*

4. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Tertiary amines are more basic than corresponding secondary and primary amines in gaseous state.
Reason (R) : Tertiary amines have three alkyl groups which cause +*I* effect.

Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(2022-23)*

5. IUPAC name of product formed by reaction of methyl amine with two moles of ethyl chloride is
(a) *N*,*N*-dimethylethanamine
(b) *N*,*N*-diethylmethanamine
(c) *N*-methylethanamine
(d) *N*-ethyl-*N*-methylethanamine. *(2020-21)* U

SA II (3 marks)

6. Account for the following :
(a) Aniline cannot be prepared by the ammonolysis of chlorobenzene under normal conditions.
(b) *N*-ethylethanamine boils at 329.3 K and butanamine boils at 350.8 K, although both are isomeric in nature.
(c) Acylation of aniline is carried out in the presence of pyridine.

OR

Convert the following :
(a) Phenol to *N*-phenylethanamide
(b) Chloroethane to methanamine
(c) Propanenitrile to ethanol *(Term II, 2021-22)*

7. What happens when reactions :
(a) *N*-ethylethanamine reacts with benzenesulphonyl chloride.
(b) Benzyl chloride is treated with ammonia followed by the reaction with chloromethane.
(c) Aniline reacts with chloroform in the presence of alcoholic potassium hydroxide.
(Term II, 2021-22) An

8. Arrange the following in increasing order of property specified :
(i) Aniline, ethanamine, 2-ethylethanamine (solubility in water)
(ii) Ethanoic acid, ethanamine, ethanol (boiling point)
(iii) Methanamine, *N*,*N* - dimethylmethanamine and *N*-methylmethanamine (basic strength in aqueous phase) *(2020-21)* Ap

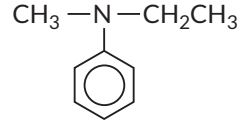
9. (i) Give a chemical test to distinguish between *N*-methylethanamine and *N*, *N*-dimethylethanamine.
(ii) Write the reaction for catalytic reduction of nitrobenzene followed by reaction of product so formed with bromine water.
(iii) Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why?
(2020-21)

9.9 Chemical Reactions (Diazonium salts)

SA II (3 marks)

10. Give reasons for any 3 of the following observations:
(a) Aniline is acetylated before nitration reaction.
(b) pK_b of aniline is lower than the *m*-nitroaniline.
(c) Primary amine on treatment with benzenesulphonyl chloride forms a product which is soluble in NaOH however secondary amine gives product which is insoluble in NaOH.
(d) Aniline does not react with methyl chloride in the presence of anhydrous $AlCl_3$ catalyst.
(2022-23) Ap

11. (a) Write the IUPAC name for the following organic compound :



(b) Complete the following :

$$C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{Br_2/H_2O} B \xrightarrow[273-278\,K]{NaNO_2/HCl} C \xrightarrow[\Delta]{HBF_4} D$$

(Term II, 2021-22)

Detailed SOLUTIONS

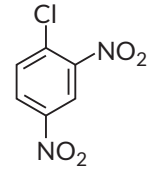
Previous Years' CBSE Board Questions

1. (a) $(C_2H_5)_2CHNH_2$ is a primary amine.

2. H_3CH_2C, H_3CH_2C > N—CH_3

IUPAC name : *N*-Ethyl-*N*-methylethanamine

Answer Tips
➲ The largest alkyl group forms a part of the aminoalkane while the smaller alkyl groups are considered as substituents.

3. 
2, 4-Dinitrochlorobenzene

4. *N*-Methylpropan-2-amine (2° amine)

5. H_3C, H_3C > N—CH_2CH_3

N,*N*-Dimethylethanamine

6. 2, 4, 6-Tribromoaniline

7. (b): When amide is treated with NaOH or KOH and Br_2, amine with one less carbon atom is obtained. The reaction is called as Hoffmann bromamide reaction.

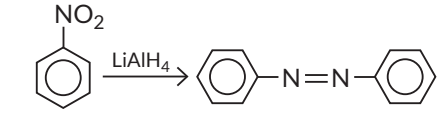
$$CH_3CONH_2 + 4NaOH + Br_2 \longrightarrow CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

8. (c): Alkyl halides when treated with ethanolic solution of NH_3 give a mixture of primary, secondary and tertiary amines.

$$R{-}X \xrightarrow{NH_3} \underset{\textit{pri}\text{-amine}}{R{-}NH_2} \xrightarrow{R-X} \underset{\textit{sec}\text{-amine}}{R_2NH} \xrightarrow{R-X} \underset{\textit{tert}\text{-amine}}{R_3N}$$

Thus it is not a suitable method.

9. (a): $LiAlH_4$ reduces aliphatic nitro compounds to amines, but converts aromatic nitro compounds such as nitrobenzene to produce azo compounds.



10. (c): $CH_3CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

11. The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

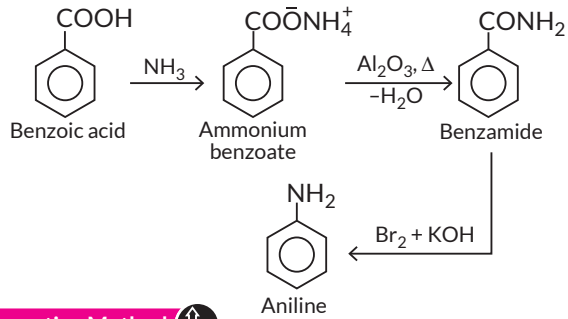
$$R{-}X \xrightarrow[-HX]{NH_2} R{-}NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$$

12. $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{(B)}{CH_3NH_2}$

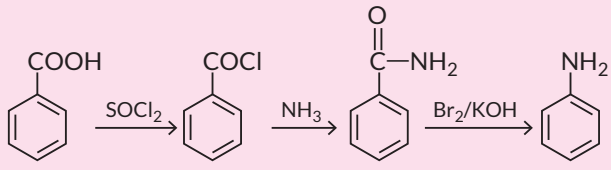
Key Points

- In Hoffmann degradation, there is one carbon atom less in product.

13.



Alternative Method



14. $\underset{\text{Acid amide}}{R{-}CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{1° amine}}{R{-}NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

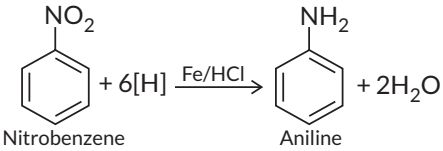
15. $\underset{\text{Ethanenitrile}}{CH_3CN} + 4[H] \xrightarrow{Na + C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$

16. $CH_3Br \xrightarrow{KCN} \underset{A}{CH_3CN} \xrightarrow{LiAlH_4} \underset{B}{CH_3CH_2NH_2}$

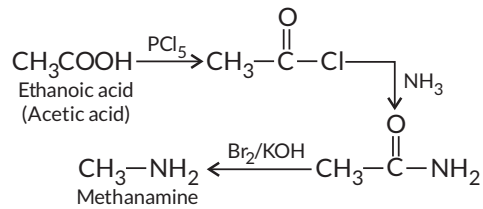
Key Points

- In this reaction, the alkyl halide is converted to primary amine having one carbon atom more than the parent alkyl halide.

17. (i)



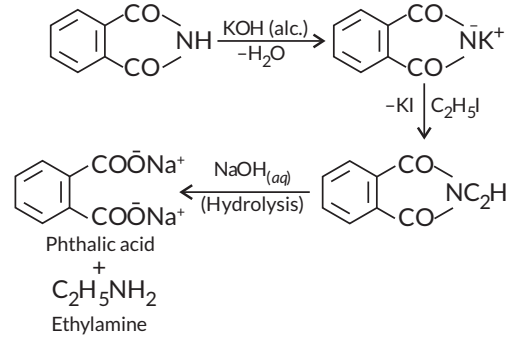
(ii)



18. (a) $(H_3CH_2C)_2N{-}CH_3$

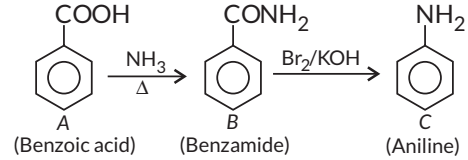
IUPAC name : *N*-Ethyl-*N*-methylethanamine

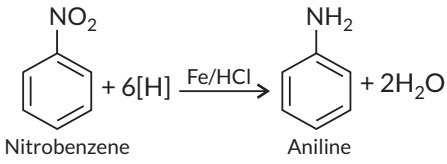
(b) (i)

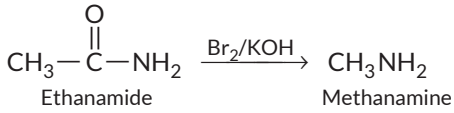


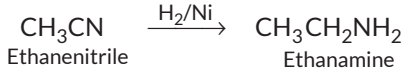
(ii) $\underset{\text{Alkyl amide}}{R{-}CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{1° amine}}{R{-}NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

19. Formula of the compound '*C*' indicates it is an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound '*B*' so compound '*B*' can be an amide. As '*B*' is obtained from compound '*A*' by reaction with ammonia followed by heating so, compound '*A*' could be an aromatic acid. Formula of compound '*C*' shows it to be aniline, then '*B*' is benzamide and compound '*A*' is benzoic acid. The sequence of reactions can be written as follows :



20. (i) 

(ii) 

(iii) 

21. CH_3OH has higher boiling point than CH_3NH_2. The hydrogen bonding in alcohols is stronger than that of amines because oxygen is more electronegative than nitrogen.

22. Decreasing order of boiling points of given compounds :
Butanol > butanamine > butane

Concept Applied

- Boiling point increases with increase in extent of hydrogen bonding.

23. Primary amines ($R - NH_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So, primary amines boil at a higher temperature than tertiary amines.

24. Increasing order of boiling points :
$(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$
Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of primary amines because oxygen is more electronegative than nitrogen.

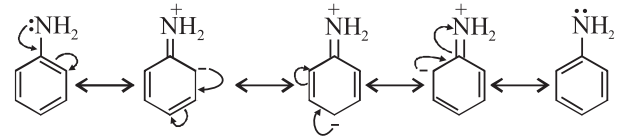
25. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$
1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

26. Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

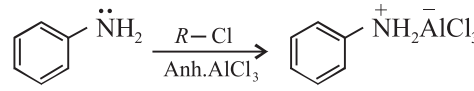
27. (i) $C_6H_5NH_2 < (CH_3)_2NH < CH_3NH_2$
1° amines are more soluble in water than 2° amines. Aniline is least soluble due to large hydrophobic benzene ring.
(ii) 1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen. The degree of association due to hydrogen bonding and hence the boiling point increase as $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$.

28. (c): Aliphatic amines are stronger bases than aromatic amines and ammonia due to $+I$ effect of alkyl group leading to high electron density on nitrogen atom. On the other hand, aromatic amines are weaker bases than even ammonia due to electron withdrawing nature of aryl group. Thus, aniline is least basic.

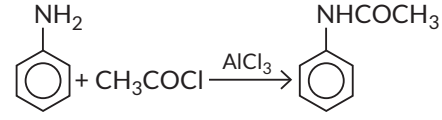
29. (b): Aniline undergoes electrophilic substitution reactions. $—NH_2$ group is *ortho* and *para* directing and a powerful activating group.



Aniline is a Lewis base, it reacts with Lewis acid used as catalyst in alkylation or acylation reaction. Due to the presence of a positive charge on N-atom in the salt, the group $-\overset{+}{N}H_2AlCl_3^-$ acts as strong deactivating group for electrophilic substitution reaction. Hence, aniline does not undergoes Friedel—Crafts reaction.



30. (c): Acetylation of aniline gives monosubstituted product as the substitution takes place at N-atom.



$-NHCOCH_3$ has less activating effect than amino group as the lone pair of electrons on nitrogen atom in $-NHCOCH_3$ is less available for donation to benzene ring due to the presence of electron withdrawing carbonyl group $\left(\begin{matrix}O\\ \|\\ —C—\end{matrix}\right)$ while lone pairs are available in case of aniline.

31. (c): $(C_2H_5)_2NH$ is more basic than $(C_2H_5)_3N$ and has less $+I$ effect in aqueous solution due to less steric hindrance as compared to $(C_2H_5)_3N$.

32. (a): $\underset{\text{(Aniline)}}{C_6H_5NH_2} + CHCl_3 + 3KOH \xrightarrow{\text{Heat}}$

$\underset{\substack{(A)\\ \text{Phenylisocyanide}}}{C_6H_5NC} + \underset{(B)}{3KCl} + \underset{(C)}{3H_2O}$

It is a carbylamine reaction.
Hence, product *A* is phenylisocyanide.

33. (b): The order of basicity of the given compounds is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$.
There is a subtle interplay of the inductive effect, solvation effect and steric hindrance of alkyl groups which decides the basic strength of alkyl amines in the aqueous state.

Commonly Made Mistake

- Order of basicity :
  In gaseous phase : 3° > 2° > 1° amine > NH_3
  In aqueous phase : $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.

34. In case of small alkyl groups like $—CH_3$ the order of basicity is secondary amine > primary amine > tertiary amine due to solvation effect and $+I$ effect of $—CH_3$ group.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

pK_b 3.27 3.38 4.22

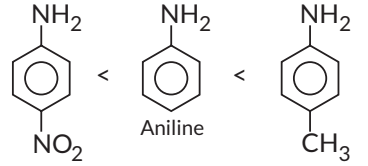
35. Decreasing order of basic strength is
$C_2H_5NH_2 > (CH_3)_3N > C_6H_5NH_2$

36. $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$

37. In aqueous solution, 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric hindrance.

38. The decreasing order of basic strength in aqueous solution is
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

39.



p-nitroaniline *p*-toluidine

Electron withdrawing group ($-NO_2$) on benzene ring decreases the basicity and electron donating group ($—CH_3$) on benzene ring increases the basicity of compound.

40. $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$
$C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine $C_6H_5CH_2NH_2$ due to lone pair of nitrogen which is in conjugation with benzene ring. But due to $+I$ effect of $—CH_3$ group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$.

41. Increasing order of basic strength in gaseous state is as follows :
$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5N(CH_3)_2$
As the number of $—CH_3$ groups ($+I$ effect) attached to nitrogen increases, its basicity will increase.

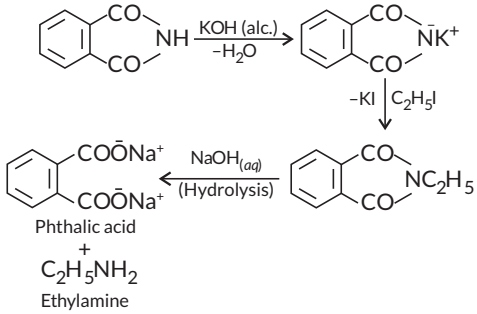
42. CH_3NH_2 is more basic than $C_6H_5NH_2$ because in aniline the lone pair of electrons on nitrogen are involved in resonance.

43. (a) Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.

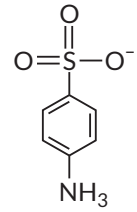
$RNH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow R—N\equiv C + 3KCl + 3H_2O$

It is the test for primary amines.

(b) Gabriel phthalimide synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.

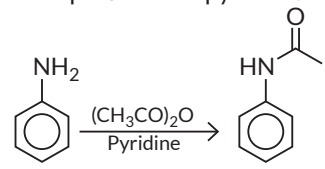


44. (i)



Sulphanilic acid
(Zwitter ion)

(ii) Activating effect of $—NH_2$ group in aniline can be controlled by protecting $—NH_2$ group by acetylation with acetic anhydride in presence of pyridine.



45. (i) Decreasing order of basic strength in aqueous solution:
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$

(ii) Increasing order of solubility in water :
$C_2H_5NH_2 > (C_2H_5)_2NH > C_6H_5NH_2$

1° amines are more soluble in water than 2° amines. Aniline is least soluble in water due to large hydrophobic benzene ring.

(iii) Decreasing order of pK_b value :
$C_6H_5NH_2 > NH_3 > C_2H_5NH_2$

Key Points

➲ When the alkyl group is bigger than $—CH_3$ group, there will be some steric hindrance to H-bonding. As a result, stability due to $+I$ effect predominates over the stability due to H-bonding, and hence 3° amines become more basic than 1° amines.

46. (i) Increasing order of basic strength is
$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(ii) Stronger the base, lower will be its pK_b value. Hence, the decreasing order of pK_b values :
$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

47. **(i) (b) :** $CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

(ii) (d) : $C_6H_5SO_2Cl$ is Hinsberg reagent.

(iii) (a) : $(CH_3)_2NH$ is strongest base in aqueous solution.

(iv) (c) : $R—X \xrightarrow[-HX]{NH_2} R—NH_2 \xrightarrow[-HX]{R—X} R_2NH \xrightarrow[-HX]{R—X} R_3N \xrightarrow{R—X} R_4N^+X^-$

OR

(b) : Order of boiling points in amines is
1° > 2° > 3°
3° amines have lower boiling point due to branching.

48. (b): Primary amines when warmed with chloroform and alcoholic solution of KOH produce isocyanides or carbylamines which have foul smell.

49. $CH_3CH_2CH_2NH_2 \xrightarrow[alc.\ NaOH]{CHCl_3} \underset{(Foul\ smell)}{CH_3CH_2CH_2NC}$

50. $C_6H_5NO_2 \xrightarrow{Fe + HCl} \underset{(A)}{C_6H_5NH_2} \xrightarrow[0\text{-}5°C]{NaNO_2 + HCl} \underset{(B)}{C_6H_5N_2^+Cl^-}$

51. $\underset{\text{Bromomethane}}{CH_3—Br} \xrightarrow{HCN} CH_3—CN \xrightarrow{Ni/H_2} CH_3CH_2NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$

52. Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali.

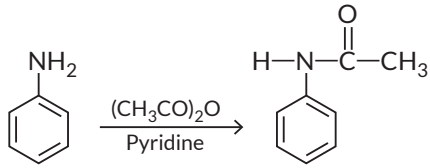
$RNH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow R—N \equiv C + 3KCl + 3H_2O$

It is the test for primary amines.

53. When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(CH_3)_2NH$ forms insoluble *N*, *N*-dialkylbenzene sulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.

Alternative Method

➲ Secondary amine on reaction with nitrous acid gives oily nitrosoamine while 3° amine forms water soluble nitrite.

54. 

Aniline — *N*-Phenylethanamide (Acetanilide)

55. Methyl amine (CH_3NH_2) is more basic than ammonia because of the presence of electron donating methyl group (+*I* effect), which increases the electron density on nitrogen atom.

56. $CH_3(C_6H_4)\ NH_2$ is more basic than $C_6H_5NH_2$ due to electron releasing nature of methyl group which pushes electrons towards nitrogen.

57. (a) $CH_3—N(—C_6H_5)—CH_2CH_3$

N-Ethyl-*N*-methylbenzenamine or *N*-Ethyl-*N*- methylamiline

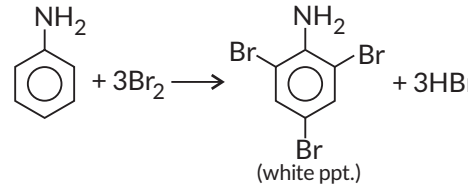
(b) $C_6H_5NO_2 \xrightarrow{Sn/HCl} \underset{(A)}{C_6H_5NH_2} \xrightarrow{Br_2/H_2O} \underset{(B)}{2,4,6\text{-tribromoaniline}} + 3HBr$

58. (i) Aniline being an aromatic primary amine on treatment with $HNO_2[NaNO_2 + HCl\ (dil.)]$ at 273–278 K followed by treatment with an alkaline solution of β-naphthol gives an orange coloured azo dye. Ethanamine does not give this test.

(ii) Aniline gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test.

59. (i) When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smelling ethyl isocyanide. Diethylamine does not give this test.

(ii) Aniline gives white or brown precipitate with bromine water.



(white ppt.)

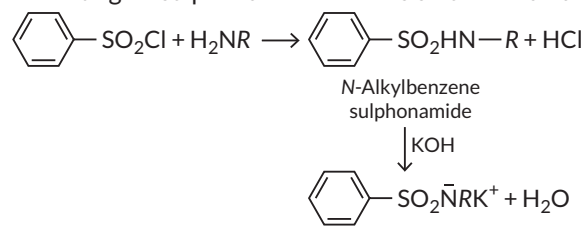
Methylamine does not react with bromine water.

60. (i) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta*-directing group. Hence, the incoming electrophile goes to *m*-position.

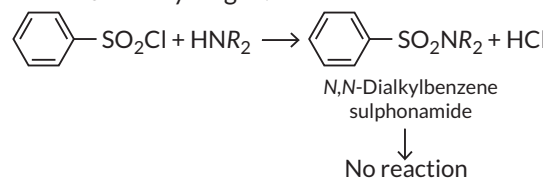
(ii) In aqueous solution, 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric reasons.

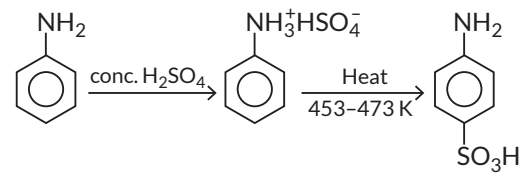
61. (a) Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

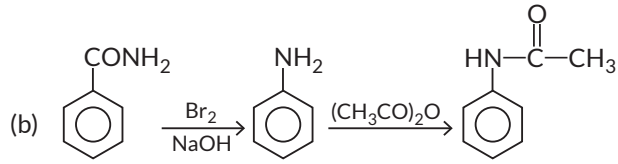
(b) Primary amines react with benzene sulphonyl chloride to give sulphonamide which is soluble in alkali.



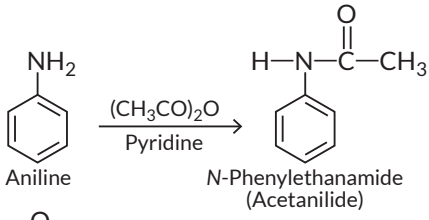
It dissolves in alkali due to the presence of acidic hydrogen on N-atom. Secondary amine reacts with benzene sulphonyl chloride to give *N*,*N*-dialkyl benzene sulphonamide which is insoluble in alkali due to the absence of acidic hydrogen.



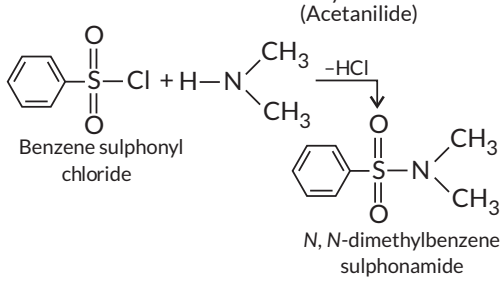
62. (a) 

(b) 

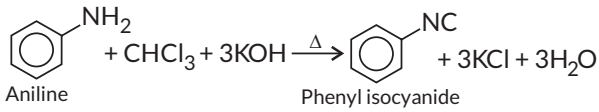
63. (i)



(ii)



64. (a) Aniline undergoes isocyanide test (carbylamine reaction) whereas, *N*, *N* – dimethylaniline does not.



Key Points

➲ Only 1° amines give positive carbylamine test.

(b) Stronger the base, lower will be the pK_b value.

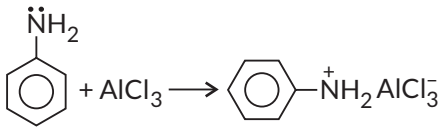
$C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$

pK_b 3.29 4.63 9.38

Commonly Made Mistake

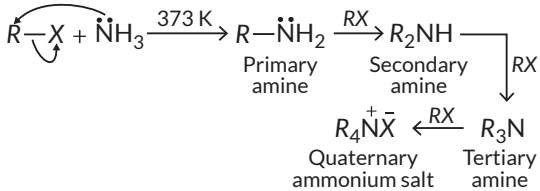
➲ pK_b is inversely proportional to basic strength.

65. (i) In Friedel — Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel — Crafts reaction.

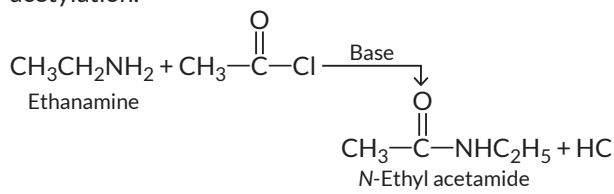


(ii) In aqueous solution, 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric hindrance.

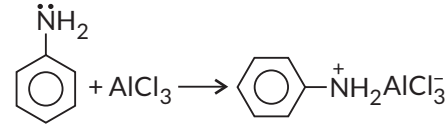
66. (i) **Ammonolysis :** Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



(ii) **Acetylation of amines :** The process of introducing an acetyl group ($CH_3—\overset{O}{\overset{\|}{C}}—$) into a molecule is called acetylation.



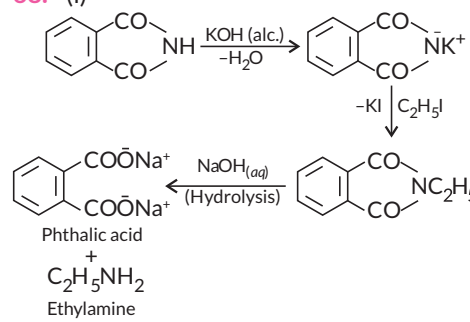
67. (i) In Friedel — Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel — Crafts reaction.



(ii) In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in $CH_3—NH_2$, +*I* effect of $—CH_3$ group increases the electron density on the N-atom.

Therefore, aniline is a weaker base than methylamine and hence, its pK_b value is higher than that of methylamine.

68. (i)



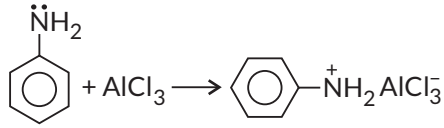
(ii) $CH_3NH_2 \xrightarrow[alc.\ KOH]{CHCl_3} CH_3NC$

(iii) $\underset{\text{Alkyl amide}}{R—CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{1° amine}}{R—NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$

69. (i) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

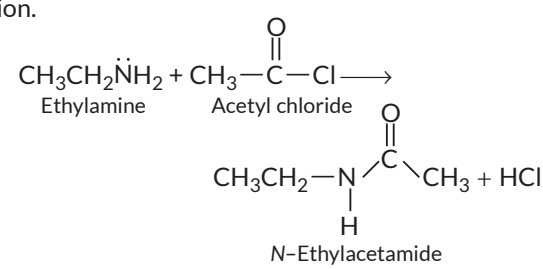
$R—X \xrightarrow[-HX]{NH_2} R—NH_2 \xrightarrow[-HX]{R—X} R_2NH \xrightarrow[-HX]{R—X} R_3N \xrightarrow{R—X} R_4N^+X^-$

(ii) In Friedel—Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel — Crafts reaction.



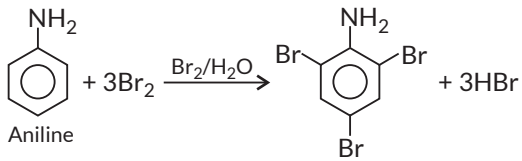
(iii) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta*-directing group. Hence, the incoming electrophile goes to *m*-position.

70. (i)



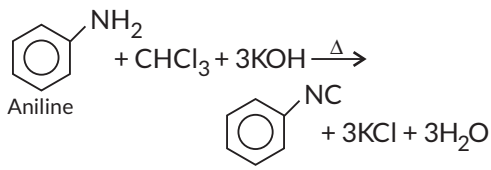
Ethylamine — Acetyl chloride — *N*–Ethylacetamide

(ii) Aniline gives white precipitates of 2,4,6-tribromo-aniline on reaction with bromine water.



Aniline — (White ppt.) 2,4,6-Tribromoaniline

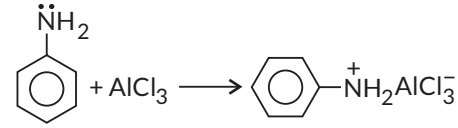
(iii) Aniline react with chloroform and ethanolic KOH to give phenyl isocyanide. This reaction is known as carbylamine reaction.



Aniline — Phenyl isocyanide (foul smell)

71. (i) In aniline, the lone pair of electrons on N-atom is delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in methylamine, $+I$-effect of $-CH_3$ group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than methylamine hence, its pK_b value is more than that for methylamine.

(ii) In Friedel – Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel – Crafts reaction.



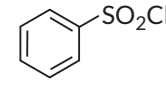
(iii) Primary amines ($R - NH_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So, primary amines boil at a higher temperature than tertiary amines.

72. (i) Basic strength in aqueous solution

$$(CH_3)_3N < CH_3—NH_2 < (CH_3)_2NH$$

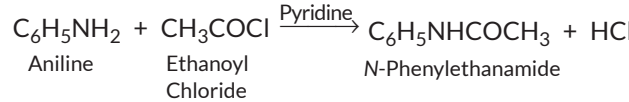
There is a subtle interplay of the inductive effect, solvation effect and steric hindrance of alkyl groups which decides the basic strength of alkyl amines in the aqueous state.

(ii) Benzenesulphonyl chloride is Hinsberg's reagent and it is used for the distinction and separation of primary, secondary and tertiary amines from a mixture.



Benzenesulphonyl chloride

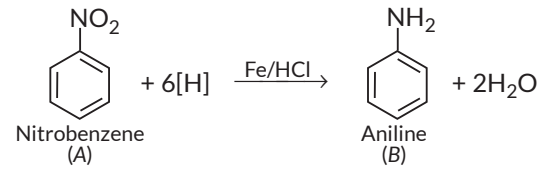
(iii) Acylation of amines is a nucleophilic substitution reaction. This reaction occurs in the presence of a base stronger than amine like pyridine. It removes HCl formed in the reaction and shifts the equilibrium to the right hand side.



Aniline — Ethanoyl Chloride — *N*-Phenylethanamide

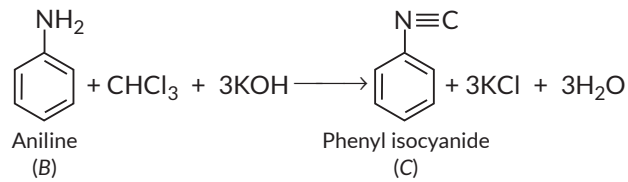
73. Nitro group ($-NO_2$) is reduced to $-NH_2$ group by treatment of iron scrap with HCl.

Molecular formula of *B* is C_6H_7N, so it may be aniline.



Nitrobenzene (*A*) — Aniline (*B*)

Aniline on reaction with $CHCl_3$ and alcoholic KOH, produces phenyl isocyanide.



Aniline (*B*) — Phenyl isocyanide (*C*)

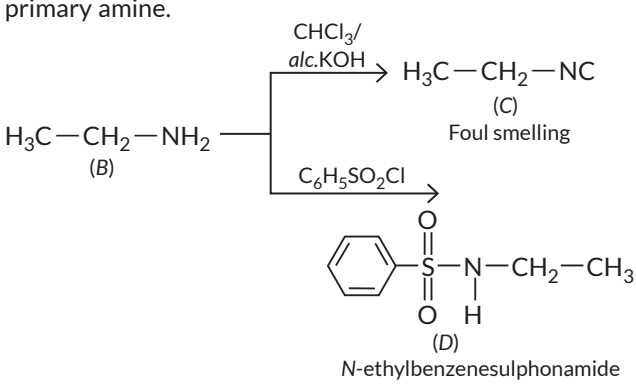
74. (i) Ethylamine forms intermolecular hydrogen bonding with water which makes it soluble in water. Aniline has a hydrophobic part C_6H_5— which makes it insoluble in water.

(ii) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta*-directing group. Hence, the incoming electrophile goes to *m*-position.
(iii) Amines behave as nucleophiles due to the presence of unshared electron pair.

75.

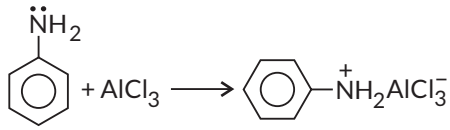
$$\underset{(A)}{H_3C-CH_2-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[\Delta]{Br_2/KOH} \underset{(B)}{H_3C-CH_2-NH_2}$$

(Hofmann degradation)
As, '*B*' reacts with $CHCl_3$/alc. KOH this means it is a primary amine.



N-ethylbenzenesulphonamide

76. (a) Ethanamine is more basic than aniline because in aniline lone pair of electrons on nitrogen are involved in resonance.
(b) In Friedel – Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel – Crafts reaction.



(c) Aromatic 1° amines such as aniline, toluidine, etc. cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

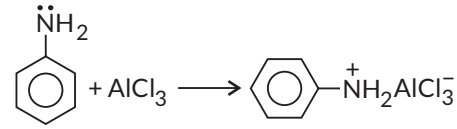
77. (a) $CH_3NH_2 + C_6H_5COCl \longrightarrow$

$$CH_3NH-\overset{O}{\overset{\|}{C}}-C_6H_5$$

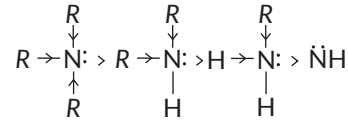
N-Methylbenzamide

(b) Stronger the base, lower will be its pK_b value. Hence increasing order of pK_b values is,
$(C_2H_5)_2NH < C_2H_5NH_2 < NH_3 < C_6H_5NH_2$

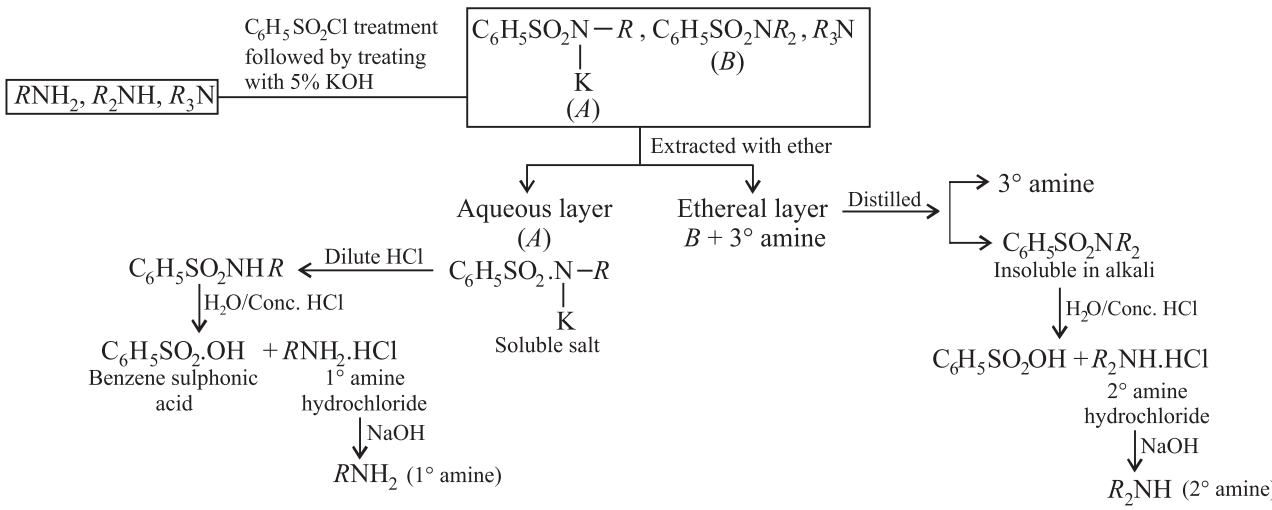
78. (i) In Friedel – Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel – Crafts reaction.



(ii) Aromatic 1° amines such as aniline, toluidine, etc. cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.
(iii) Amines and ammonia are Lewis bases due to the presence of lone pair of electrons on them. As aliphatic amines have alkyl group which shows +*I* effect and increases electron density on amines hence and behave as stronger bases.



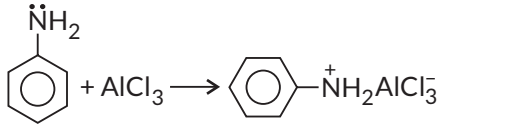
79. Primary, secondary and tertiary amines can be distinguished by Hinsberg reagent.



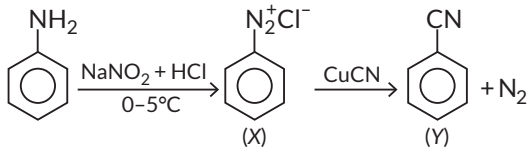
80. (a) (i) Methylamine gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test.

(ii) Aniline being an aromatic primary amine on treatment with HNO_2[$NaNO_2$ + HCl (*dil.*)] at 273–278 K followed by treatment with an alkaline solution of β-naphthol gives an orange coloured azo dye. Ethylamine does not give this test.

(b) In Friedel — Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel — Crafts reaction.



81. (a)



(b) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta*-directing group. Hence, the incoming electrophile goes to *m*-position.

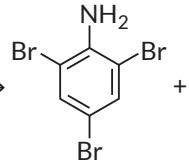
82. (i) After acetylation of aniline, acetanilide is formed in which due to the presence of $-\overset{O}{\overset{\|}{C}}-CH_3$ group having *–I* effect, electron density on N-atom decreases and hence, activation effect of aniline gets reduced.

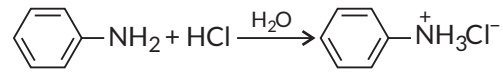
Answer Tips

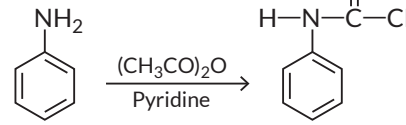
➲ $-\overset{O}{\overset{\|}{C}}-CH_3$ group exerts *–I*-effect on adjacent —NH_2 group.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$ because in aniline the lone pair of electrons on nitrogen are involved in resonance.

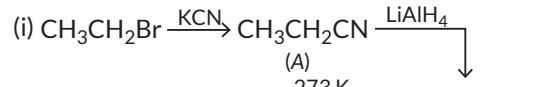
(iii) Nitration is carried out with conc. HNO_3 in the presence of conc. H_2SO_4. In the presence of these acids, the $-NH_2$ group of aniline gets protonated and is converted into $-\overset{+}{N}H_3$ group. This positively charged group acts as a strong electron withdrawing and *meta*-directing group. Hence, the incoming electrophile goes to *m*-position.

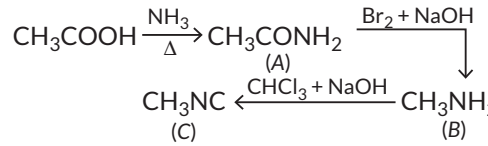
83. (i) $C_6H_5NH_2 + Br_{2(aq)} \longrightarrow$  + 3HBr

(ii) 

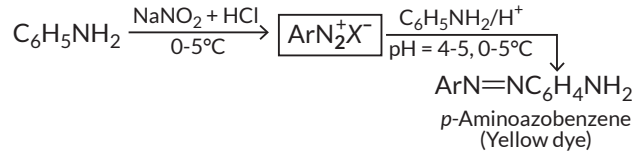
(iii) 

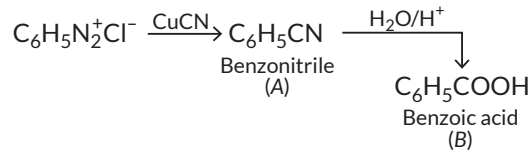
Aniline — *N*-Phenylethanamide (Acetanilide)

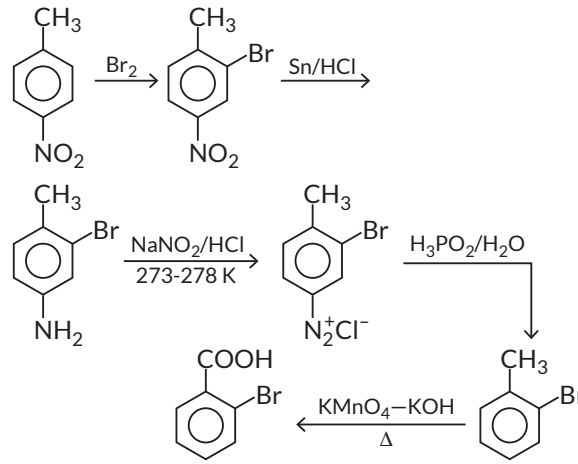
84. (i) 

(ii) 

85. **(b):**



86. 

87. 

Commonly Made Mistake

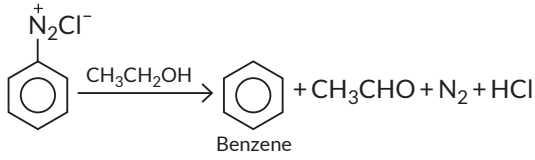
➲ —CH_3 is *o*- and *p*- directing while —NO_2 is *m*-directing and deactivating group. So, the product is formed in accordance with these conditions.

88. $C_6H_5N_2^+Cl^- + C_2H_5OH \xrightarrow{\text{Reduction}}$ $C_6H_6 + CH_3CHO + N_2\uparrow + HCl$

Benzenediazonium chloride — Benzene — Ethanal

89. $C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow$ $C_6H_6 + N_2 + H_3PO_3 + HCl$

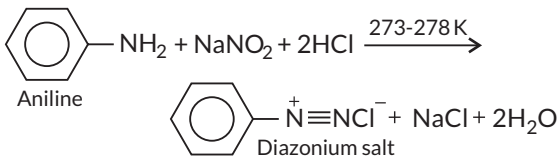
90. Diazotisation reaction.

91. (i) 

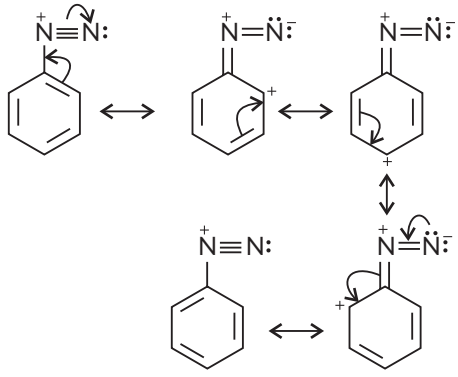
(ii) $CH_3CH_2Br \xrightarrow{alc.KOH} CH_2=CH_2 \xrightarrow{aq.\ KCN}$
Bromoethane

$CH_3-CH_2-C\equiv N \xrightarrow{H_2/Pd} CH_3-CH_2-CH_2-NH_2$
Propanamine

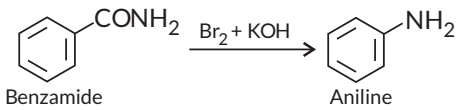
92. (a) Diazotisation :

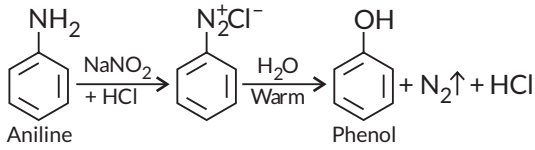


(b) Diazonium salts carry a nitrogen atom with a positive charge. This positive charge is well dispersed in aromatic diazonium salts through resonance as shown below :



Such a charge delocalisation is not possible in aliphatic diazonium salts and hence they are less stable than aromatic diazonium salts.

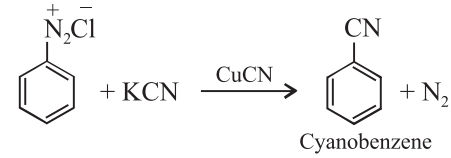
93. (i) 

(ii) 

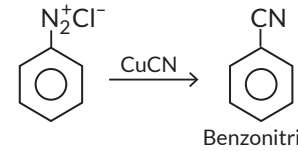
94. (i) $C_6H_5NO_2 \xrightarrow{Sn+HCl} \underset{A}{C_6H_5NH_2} \xrightarrow{NaNO_2+HCl} \underset{B}{C_6H_5N_2^+Cl^-} \xrightarrow{H_2O} \underset{C}{C_6H_5OH}$

(ii) $CH_3CN \xrightarrow{H_2O/H^+} \underset{A}{CH_3COOH} \xrightarrow{NH_3} \underset{B}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{C}{CH_3NH_2}$

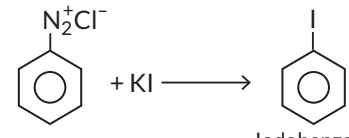
95. (a) The replacement of $-\overset{+}{N}_2\bar{Cl}$ group of benzene diazonium chloride by the nucleophiles Cl^-, Br^- and CN^- in the presence of Cu(I) ion as catalyst is called Sandmeyer reaction.
Example, benzene diazonium chloride when treated with KCN in presence of CuCN gives cyanobenzene.



(b) In aqueous solution, 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric hindrance.

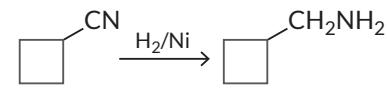
96. (i) 

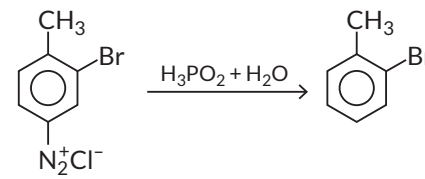
(ii) $\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2^+Cl^-} + C_2H_5OH \xrightarrow{Reduction} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$

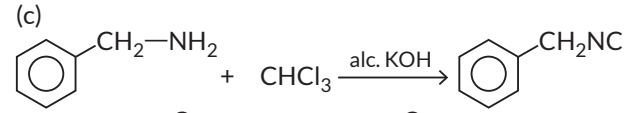
(iii) 

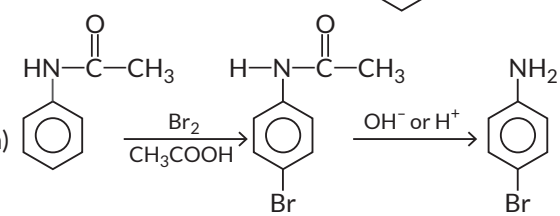
Answer Tips

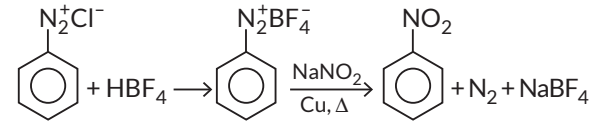
➲ In benzene diazonium chloride salt, $-N_2^+Cl^-$ group is attacked by incoming nucleophile.

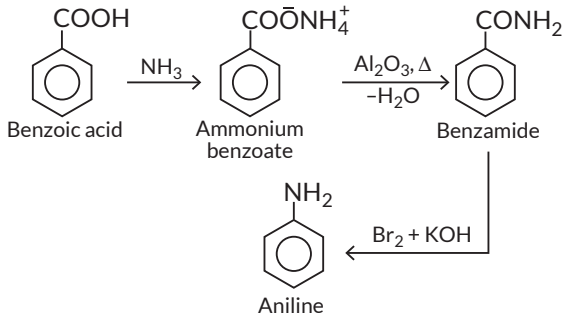
97. (a) 

(b) 

(c) 

98. (a) 

(b) 

(iii) 

99. (a) $CH_3COOH \xrightarrow[\Delta]{NH_3} CH_3CONH_2 \xrightarrow{Br_2 + NaOH} CH_3NH_2$ (B)

CH_3NC (C) $\xleftarrow{CHCl_3 + \text{alc. KOH}}$ CH_3NH_2 (B)

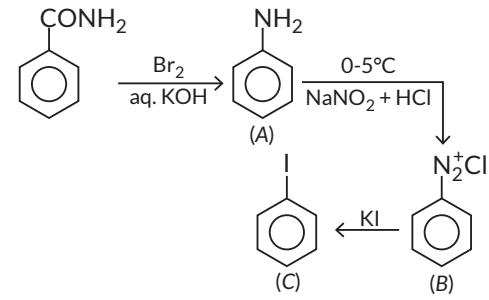
(b) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} C_6H_5NO_2$

Nitrobenzene (A)

(Reduction) $\downarrow$ Fe/HCl

$C_6H_5NHCOCH_3$ (C) $\xleftarrow[\text{Pyridine}]{CH_3COCl}$ $C_6H_5NH_2$ (B)

Acetanilide (C) — Aniline (B)

100. (i) 

(ii) $CH_3-Cl \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

(A) (B)

CH_3CH_2NC (C) $\xleftarrow[\Delta]{CHCl_3 + \text{alc. KOH}}$ $CH_3CH_2NH_2$ (B)

101. (i) $C_6H_5NO_2 \xrightarrow{Sn + HCl} C_6H_5NH_2 \xrightarrow{NaNO_2 + HCl}$

A

C_6H_5OH (C) $\xleftarrow{H_2O}$ $C_6H_5N_2^+Cl^-$ (B)

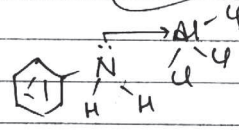
(ii) $CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

A B

CH_3CH_2OH (C) $\xleftarrow[273\ K]{HNO_2}$

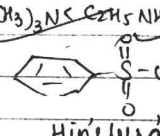
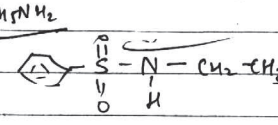
102.

i) Aniline does not give friedel-Crafts reaction because, it donates its lone pair to the Lewis Acid used as a catalyst in the reaction. Therefore no electrophile is generated.



(ii) order of pK_b : $C_6H_5NH_2 > NH_3 > C_2H_5NH_2 > (CH_3)_3N$

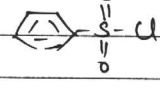
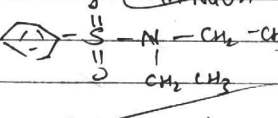
pK_b increasing order :- $(CH_3)_3N < C_2H_5NH_2 < NH_3 < C_6H_5NH_2$

(iii) $CH_3CH_2NH_2$ +  → 

1° amine

Hinsberg's reagent

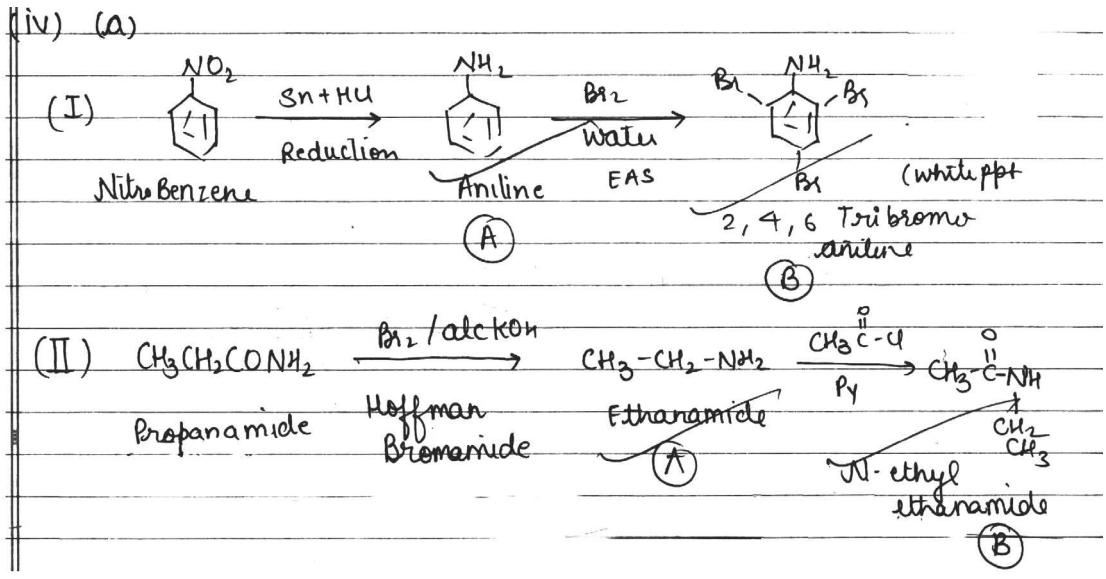
N-ethyl benzene Sulphonamide (Soluble in NaOH)

$(CH_3-CH_2)_2NH$ +  → 

2° amine

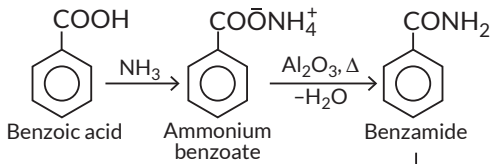
N,N diethyl benzene Sulphonamide (water Insoluble in NaOH)

the compound formed with 1° amine is soluble in NaOH due to the presence of Acidic H whereas compound formed with 2° amine is insoluble in NaOH due to absence of any Acidic H

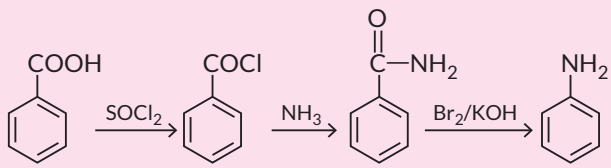


[Topper's Answer, 2022]

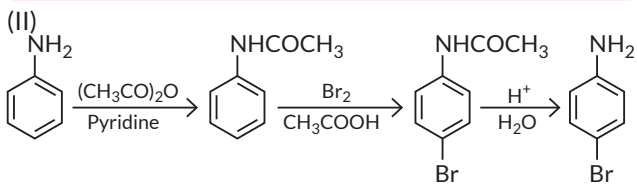
(b) (I)



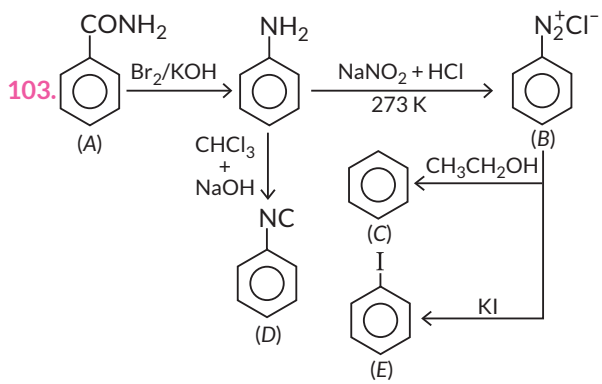
Alternative Method



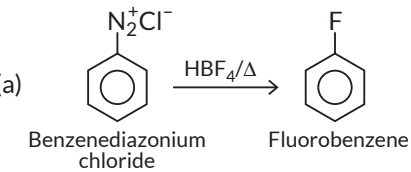
(II)



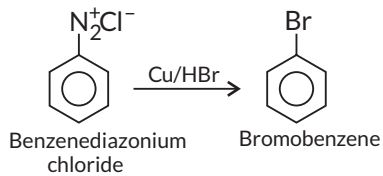
103.



104. (i) (a)



(b)



(ii) (a) $C_6H_5NO_2 \xrightarrow{Sn + HCl} \underset{A}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2 + HCl} \underset{B}{C_6H_5N_2^+Cl^-} \xrightarrow{H_2O} \underset{C}{C_6H_5OH}$

(b) $CH_3Cl \xrightarrow{KCN} \underset{A}{CH_3CN} \xrightarrow{LiAlH_4} \underset{B}{CH_3CH_2NH_2} \xrightarrow[273\ K]{HNO_2} \underset{C}{CH_3CH_2OH}$

CBSE Sample Questions

1. **(b) :** $CH_3CH_2CONH_2 + Br_2 + 4NaOH \longrightarrow$
Propanamide
$CH_3CH_2NH_2 + 2NaBr + K_2CO_3 + H_2O$
Ethanamine **(1)**

2. **(d):** *B* < *C* < *A*
In primary amine, intermolecular association due to H-bonding is maximum while in tertiary, it is minimum. **(1)**

3. **(c):** CH_3NH_2 on reaction with nitrous acid releases N_2 gas, not NO_2 gas. **(1)**

4. (a) **(1)**

5. (d): CH_3NH_2 (Methyl amine) $\xrightarrow[(-HCl)]{CH_3CH_2Cl}$ $(CH_3CH_2)NHCH_3$ $\xrightarrow[(-HCl)]{(CH_3CH_2Cl)}$ $CH_3CH_2-N(CH_3)-CH_2-CH_3$

N-Ethyl-*N*-methylethanamine **(1)**

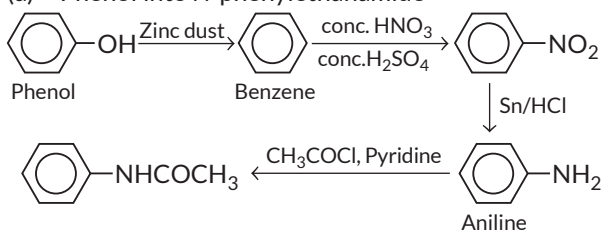
6. (a) Under the normal conditions, ammonolysis of chlorobenzene does not yield aniline as in chlorobenzene, the C—Cl bond is quite difficult to break as it acquires a partial double bond character. **(1)**

(b) Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen and one of the hydrogen of another molecule. Due to the presence of two hydrogen atoms, the intermolecular association is more in primary amines than in secondary amines where only one hydrogen atom is available for hydrogen bond formation in it. Hence, butanamine being primary amine has a higher boiling point as compared to *N*-ethyl ethanamine which is a secondary amine. **(1)**

(c) During the acylation of aniline, a stronger base pyridine is added to remove the HCl formed during the reaction and to shift the equilibrium to the product side to get the better yield. **(1)**

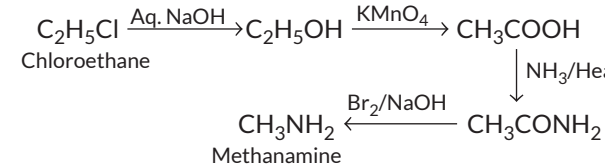
OR

(a) Phenol into *N*-phenylethanamide



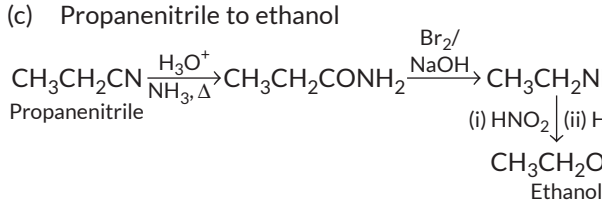
(1)

(b) Chloroethane to methanamine



(1)

(c) Propanenitrile to ethanol



(1)

7. (a) When *N*-ethylethanamine reacts with benzenesulphonyl chloride, *N*, *N*-diethylbenzenesulphonamide is formed. **(1)**

(b) When benzyl chloride is treated with ammonia, benzyl amine is formed which on reaction with chloromethane yields a secondary amine, *N*-methylbenzylamine. **(1)**

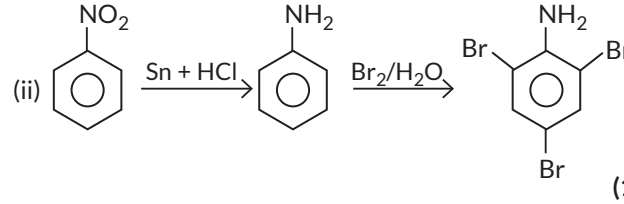
(c) When aniline reacts with chloroform in the presence of alcoholic potassium hydroxide, phenyl isocyanide or phenyl isonitrile is formed. **(1)**

8. (i) Aniline < 2-ethylethanamine < ethanamine (solubility in water) **(1)**

(ii) Ethanamine < ethanol < ethanoic acid (boiling point) **(1)**

(iii) *N*,*N*-Dimethylmethanamine < methanamine < *N*-methylmethanamine (basicity strength in aqueous phase). **(1)**

9. (i) *N*-methylethanamine is a secondary amine. When it reacts with benzenesulphonyl chloride, it forms *N*-ethyl-*N*-methylsulphonamide while *N*,*N*-dimethyl ethanamine is a tertiary amine, it does not react with benzenesulphonyl chloride. **(1)**

(ii) 

(1)

(iii) Butan-1-ol is more soluble in water because electronegativity of oxygen (3.5) is more than that of nitrogen (3.0) and therefore, alcohols form stronger hydrogen bonds as compared to amines. **(1)**

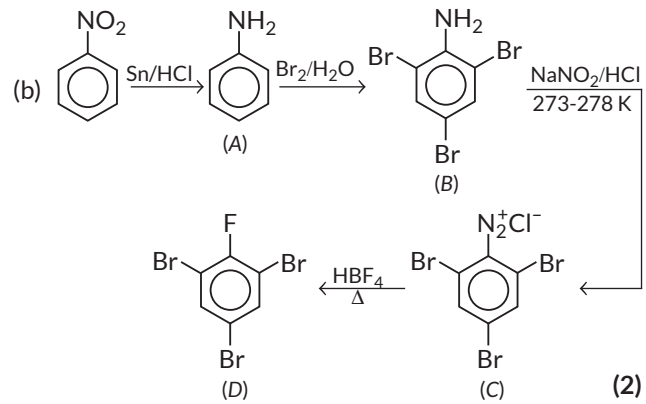
10. (a) Aniline is acetylated before nitration reaction in order to avoid formation of tarry oxidation products and protecting the amino group, so that *p*-nitro derivative can be obtained as major product. **(1)**

(b) pK_b of aniline is lower than the *m*-nitro aniline. The basic strength of aniline is more than *m*-nitroaniline. Presence of electron withdrawing group decreases basic strength. pK_b value is inversely proportional to basic strength. **(1)**

(c) Due to the presence of acidic hydrogen in the *N*-alkylbenzenesulphonamide formed by the treatment of primary amines, it is soluble in NaOH. Secondary amine forms *N*,*N*-dialkybenzenesulphonamide which due to the absence of acidic hydrogen on N-atom does not dissolve in NaOH. **(1)**

(d) Aniline does not react with methylchloride in the presence of $AlCl_3$ catalyst, because aniline is a base and $AlCl_3$ is Lewis acid which lead to formation of salt. **(1)**

11. (a) *N*-Ethyl-*N*-methylbenzamine or *N*-Ethyl-*N*-methylaniline **(1)**

(b) 

(2)

Self Assessment

Case Based Questions (5 marks)

1. Read the passage given below and answer the following questions :

A mixture of two aromatic compounds (*A*) and (*B*) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound (*A*), when heated with alcoholic solution of KOH produce C_7H_5N (*C*) associated with unpleasant odour.

(i) What is *A*?

(a) $C_6H_5NH_2$ (b) $C_6H_5CH_3$

(c) C_6H_5CHO (d) None of these

(ii) The reaction of (*A*) with alcoholic solution of KOH to produce (*C*) of unpleasant odour is called

(a) Sandmeyer reaction

(b) Carbylamine reaction

(c) Ullmann reaction

(d) Reimer-Tiemann reaction.

(iii) The alkaline aqueous layer (*B*) when heated with chloroform and then acidified give a mixture of isomeric compounds of molecular formula $C_7H_6O_2$. (*B*) is

(a) C_6H_5CHO (b) C_6H_5COOH

(c) $C_6H_5CH_3$ (d) C_6H_5OH

(iv) In the chemical reaction,

$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow (X) + (Y) + 3H_2O$,

the compounds (*X*) and (*Y*) are respectively

(a) C_2H_5NC and KCl

(b) C_2H_5CN and KCl

(c) $CH_3CH_2CONH_2$ and KCl

(d) C_2H_5NC and K_2CO_3

(v) Direct nitration of an aromatic compound (*A*) is not feasible because

(a) the reaction cannot be stopped at the mononitration stage

(b) a mixture of *o*, *m* and *p*-nitroaniline is always obtained

(c) nitric acid oxidises most of the aromatic compound to give oxidation products along with only a small amount of nitrated products

(d) all of the above.

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

2. Assertion : Hoffmann bromamide reaction is given by primary amide.

Reason : Primary amines are more basic than secondary amines.

3. Assertion : Acetanilide is less basic than aniline.

Reason : Acetylation of aniline results in decrease of electron density on nitrogen.

Multiple Choice Questions (1 mark)

4. Which of the following methods of preparation of amines will not give same number of carbon atoms in the chain of amines as in the reactant?

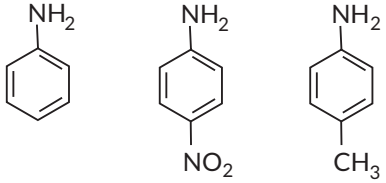
(a) Reaction of nitrile with $LiAlH_4$.

(b) Reaction of amide with $LiAlH_4$ followed by treatment with water.

(c) Heating alkyl halide with potassium salt of phthalimide followed by hydrolysis.

(d) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

5. The correct increasing order of basic strength for the following compounds is



(I) (II) (III)

(a) II < III < I (b) III < I < II

(c) III < II < I (d) II < I < III

6. The best reagent for converting 2–phenylpropanamide into 2-phenylpropanamine is _____ .

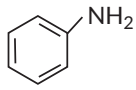
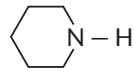
(a) excess H_2

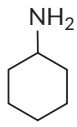
(b) Br_2 in aqueous NaOH

(c) iodine in the presence of red phosphorus

(d) $LiAlH_4$ in ether

7. Which of the following is the weakest Brönsted base?

(a)  (b) 

(c)  (d) CH_3NH_2

OR

Reaction of aniline with HNO_2 followed by treatment of dilute acid gives

(a) C_6H_5NHOH (b) C_6H_5OH

(c) $C_6H_5NHNH_2$ (d) C_6H_6

VSA Type Questions (1 mark)

8. State reasons for the following :

pK_b value for aniline is more than that for ethylamine.

9. Why is an alkylamine more basic than ammonia?

10. How will you bring about the following conversion : Aniline to chlorobenzene?

Write the chemical equation involved.

11. How is the following conversion carried out :

Aniline to *p*-hydroxyazobenzene ?

SA I Type Questions (2 marks)

12. Suggest chemical reaction for the following conversions :

(i) Aniline to benzoic acid

(ii) *n*-Hexanenitrile to 1-aminopentane

13. Account for the following :

(i) Aqueous solution of methylamine reacts with iron(III) chloride to precipitate iron(III) hydroxide.

(ii) The boiling points of amines are lower than those of corresponding alcohols.

14. (i) Give reason : Silver chloride dissolves in methylamine solution.

(ii) Write the chemical reaction for the reduction of nitroethane by $LiAlH_4$.

15. (a) The diazonium ion acts as an electrophile. Give reason.

(b) Write short note on Sandmeyer reaction.

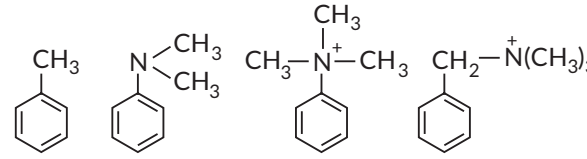
OR

(a) Complete the following series of reaction :

$$PhNH_2 \xrightarrow{A} PhN_2^+Cl^- \xrightarrow{B} PhCN \xrightarrow{C} Ph-\underset{H}{\overset{H}{C}}-NH_2$$

(b) How is aminoethane obtained from ethanal?

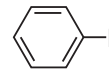
16. Give increasing order of electrophilic substitution of the following compounds :



SA II Type Questions (3 marks)

17. Complete the following with appropriate structure :

(i) 2,4-dinitroaniline $\xrightarrow[\text{2. anisole}]{\text{1. } NaNO_2 \text{ and HCl at 5°C}}$ (A)

(ii)  $\xrightarrow{HNO_2}$ (B)

18. State the reason for the following :

(i) Acetylation of aniline reduces its activation effect.

(ii) Methylamine is more basic than aniline.

(iii) How is the basic strength of aromatic amines affected by the presence of an electron releasing group on the benzene ring?

19. (a) Arrange the following in increasing order of basic strength : Aniline, *p*-nitroaniline and *p*-toluidine.

(b) Account for the observation that like ammonia, amines are good nucleophiles.

OR

Accomplish the following conversions :

(i) Benzyl chloride to 2-phenylethanamine

(ii) Aniline to *p*-bromoaniline

(iii) Benzamide to toluene

20. Explain the following observations :

(i) In aqueous solution, the K_b order is $Me_2NH > MeNH_2 > Me_3N$.

(ii) Why cannot primary aromatic amines be prepared by Gabriel phthalimide synthesis?

(iii) Tertiary amines do not undergo acylation reaction.

Case Based Questions (4 marks)

21. **Read the passage given below and answer the following questions :**

Amines are alkyl or aryl derivatives of ammonia formed by replacement of one or more hydrogen atoms. Alkyl derivatives are called aliphatic amines and aryl derivatives are known as aromatic amines. The presence of aromatic amines can be identified by performing dye test. Aniline is the simplest example of aromatic amine. It undergoes electrophilic substitution reactions in which $-NH_2$ group strongly activates the aromatic ring through delocalisation of lone pair of electrons of N-atom. Aniline undergoes

electrophilic substitution reactions. *Ortho* and *para* positions to the $-NH_2$ group become centres of high electrons density. Thus, $-NH_2$ group is *ortho* and *para*-directing and powerful activating group.

(a) How will you distinguish cyclohexylamine and aniline?

(b) What does oxidation of aniline in presence of MnO_2 and H_2SO_4 produce?

(c) What is the major product obtained by acetylation of aniline followed by nitration (conc.HNO_3 + conc.H_2SO_4) and then alkaline hydrolysis?

OR

What does aniline produce in carbylamine reaction? Write chemical equation of the reaction involved.

LA Type Questions (5 marks)

22. (i) Identify *A*, *B* and *C* in the following reactions :

(a) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2 + KOH} B \xrightarrow{CHCl_3 + NaOH} C$

(ii) (a) How are amines prepared from amides?

(b) Acylation of amines with acid chloride is carried out in presence of stronger base. Why?

23. A hydrocarbon '*A*' (C_4H_8) on reaction with HCl gives a compound '*B*' (C_4H_9Cl), which on reaction with 1 mole of NH_3 gives compound '*C*' ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound '*C*' yields an optically active alcohol, '*D*'. Ozonolysis of '*A*' gives 2 moles of acetaldehyde. Identify compounds '*A*' to '*D*'. Explain the reactions involved.

OR

(a) Write chemical equations for the following conversions :

(i) Nitrobenzene to benzoic acid.

(ii) Aniline to benzyl alcohol.

(b) Give the structures of *A*, *B* and *C* in the following reactions :

(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(ii) $C_6H_5NO_2 \xrightarrow[\Delta]{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[H_2O/H^+]{\Delta} C$

24. (a) An aromatic compound '*A*' on treatment with aqueous ammonia and heating forms compound '*B*' which on heating with Br_2 and KOH forms a compound '*C*' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds *A*, *B* and *C*.

(b) Write tests to distinguish the following pairs of compounds:

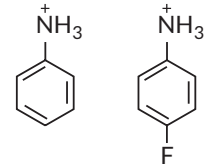
(i) Aniline and ethylamine

(ii) Ethylamine and dimethylamine

25. (i) (a) $\underset{\text{Optically active}}{C_5H_{13}N(X)} \xrightarrow[N_2]{NaNO_2/HCl} Y$ (tertiary alcohol) + other products

Find *X* and *Y*. Is *Y* optically active? Write the intermediate steps.

(b) Which of the following is more acidic and why?



(ii) Acetamide is less basic than ethanamine. Why?

Detailed SOLUTIONS

1. (i) (a): Given, mixture of (*A*) and (*B*) $\xrightarrow[+ KOH_{(aq)}]{CHCl_3}$ Organic layer (*A*) + Alkaline aqueous layer (*B*) Organic layer on treating with KOH (alc.) produces (C_7H_5N) (*C*) of unpleasant odour and thus (*C*) is C_6H_5NC. Therefore, (*A*) is $C_6H_5NH_2$.

(ii) (b): Carbylamine reaction

$$C_6H_5NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow \underset{\text{Phenyl isocyanide (C)}}{C_6H_5NC} + 3KCl + 3H_2O$$

(iii) (d): Alkaline layer on treating with $CHCl_3$ followed by acidification gives two isomers having formula ($C_7H_6O_2$). This is Reimer-Tiemann reaction and thus, (*B*) is C_6H_5OH.

$$\underset{\text{Phenol (B)}}{C_6H_5OH} + CHCl_3 + KOH \xrightarrow{H^+} \underset{\text{o-Hydroxy benzaldehyde}}{\text{OH, CHO}} + \underset{\text{p-Hydroxy benzaldehyde}}{\text{OH, CHO}}$$

(iv) (a): $CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$

This is called carbylamine reaction.

(v) (c): Direct nitration of aniline is not a feasible process because nitric acid oxidises most of aniline to give oxidation products along with only a small amount of nitrated products.

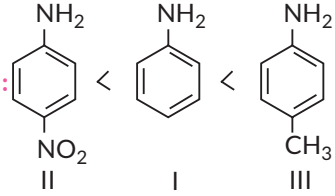
2. **(c):** Secondary amines are more basic than primary amines.

3. **(a):** The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance, which results in decrease in electron density on nitrogen hence, it is less basic than aniline.

4. **(d):** Treatment of amide with Br_2 in aqueous solution of NaOH will give an amine with one carbon atom less in number than in the reactant.

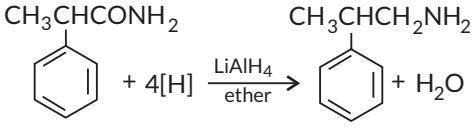
$$RCONH_2 \xrightarrow{Br_2/NaOH} RNH_2$$

5. **(d):**



Electron withdrawing group decreases the basic strength while electron releasing groups increases the basic strength of aniline.

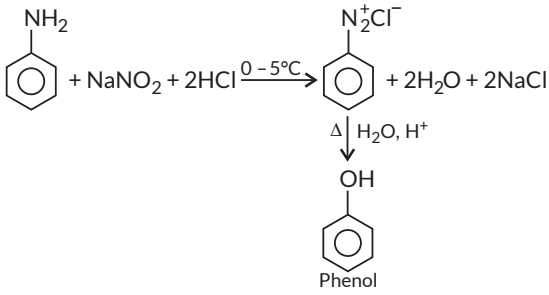
6. **(d):**



7. **(a):** Aniline is the weakest base since NH_2 is directly attached to benzene ring and the unshared electron pair on nitrogen is less available due to delocalisation. Anilinium ion obtained by accepting a proton has only two resonating structures making it less stable than aniline.

OR

(b) : $NaNO_2 + HCl \longrightarrow NaCl + HNO_2$

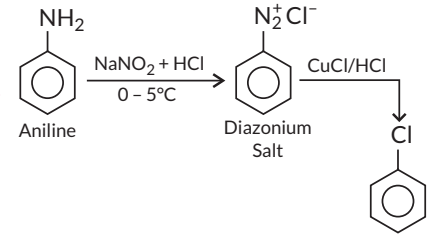


8. In aniline, the lone pair of electrons on N-atom is delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in ethylamine, $+I$-effect of $-C_2H_5$ group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than ethylamine hence, its pK_b value is more than that for ethylamine.

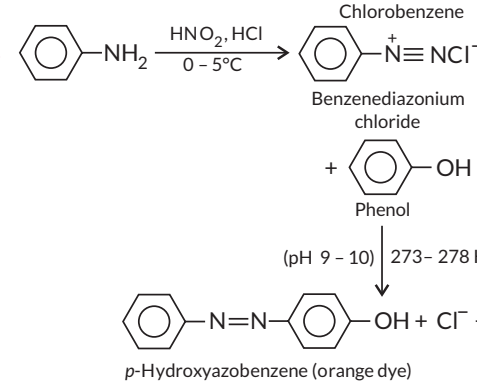
9. Electron density of N-atom increases due to the $+I$ effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

$\ddot{N}H_3$, $R \rightarrow \ddot{N}H_2$

10.



11.



12. (i) $C_6H_5NH_2 \xrightarrow[273\ K]{NaNO_2 + HCl} C_6H_5\overset{+}{N}_2Cl^-$

Aniline → Benzenediazonium chloride

$\xrightarrow[Pyridine]{Cu_2(CN)_2} C_6H_5CN \xrightarrow[hydrolysis]{H_2O/H^+} C_6H_5COOH$

Benzoic acid

(ii) $CH_3CH_2CH_2CH_2CH_2CN \xrightarrow[NH_3]{H^+/H_2O}$ *n*-Hexanenitrile

$CH_3CH_2CH_2CH_2CH_2CONH_2 \xrightarrow[\text{Hoffmann degradation}]{Br_2/NaOH}$ Hexanamide

$CH_3CH_2CH_2CH_2CH_2NH_2$ 1-Aminopentane

13. (i) Methylamine reacts with water to form methyl ammonium hydroxide which is more basic than NH_4OH and ionizes to give OH^- ions.

$$CH_3NH_2 + H_2O \longrightarrow \overset{+}{C}H_3NH_3 + OH^-$$

$$FeCl_3 + 3OH^- \longrightarrow \underset{\text{Red brown ppt.}}{Fe(OH)_3\downarrow} + 3Cl^-$$

(ii) As oxygen is more electronegative than nitrogen therefore, hydrogen bonding among alcohol molecules is stronger than among amine molecules. So, alcohols have higher boiling points than amines.

14. (i) Amines form soluble coordination compounds with Ag^+ ions. Therefore white ppt. of silver chloride is dissolved in methylamine solution.

$$\underset{\text{Silver chloride (insoluble)}}{AgCl} + 2CH_3-\ddot{N}H_2 \longrightarrow \underset{\text{Soluble complex}}{[(CH_3NH_2)_2Ag]Cl}$$

(ii) $\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 6[H] \xrightarrow[ether]{LiAlH_4} CH_3CH_2NH_2 + 2H_2O$

15. (a) Due to positive charge on electronegative nitrogen atom diazonium ion acts as an electrophile.

(b) The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion. This is called Sandmeyer reaction.

$$ArN_2^+X^- \xrightarrow[HCl]{Cu_2Cl_2} ArCl + N_2$$

OR

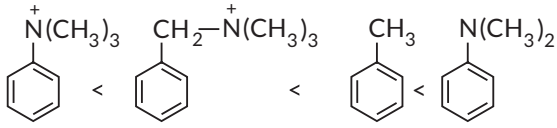
(a) $PhNH_2 \xrightarrow[0-5°C]{NaNO_2/HCl} PhN_2^+Cl^- \xrightarrow{CuCN}$

$PhCN \xrightarrow{Sn/HCl} Ph-\underset{H}{\overset{H}{C}}-NH_2$

(b) $CH_3-\underset{\text{Ethanal}}{\overset{H}{C}=O} + NH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\underset{\text{Acetaldimine}}{\overset{H}{C}=NH}$

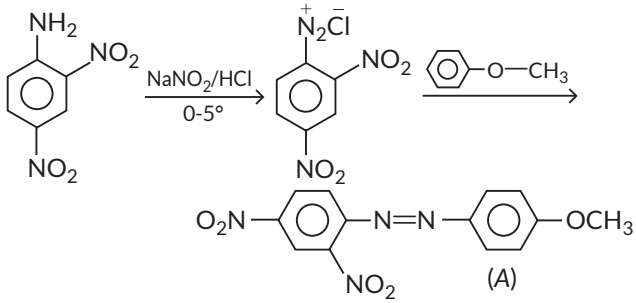
$CH_3CH_2NH_2 \xleftarrow{H_2/Ni}$ Ethanamine

16. Higher the electron density in the benzene ring, more reactive is the aromatic compound towards electrophilic substitution reaction. Now due to the presence of a lone pair of electrons on the N-atom which it can directly donate to the benzene ring, $-N(CH_3)_2$ is a much stronger electron donating group than $-CH_3$ group. The remaining two groups contain a positive charge on the N-atom and hence, act as electron withdrawing groups. But in $-N^+(CH_3)_3$ group, the positively charged N is directly attached to the benzene ring, therefore, its electron withdrawing ability is much stronger than $-CH_2N^+(CH_3)_3$. Thus, the electron density in the benzene ring increases in the order :

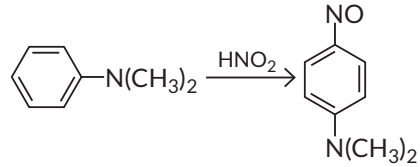


Therefore, their reactivity towards electrophilic substitution reactions also increases in the same order.

17. (i)



(ii)



18. (i) After acetylation of aniline, acetanilide is formed in which electron density on N-atom decreases due to the presence of $-COCH_3$ group, having $-R$ effect, and hence, activation effect of aniline gets reduced.

(ii) In aniline, lone pair of electrons on nitrogen atom is not free for donation because it is involved in resonance. But in case of methylamine, lone pair of electrons on nitrogen atom is free for donation. So, aniline is less basic than methylamine.

(iii) An electron releasing group increases the electron density on the amino group. As a result, the electron density or the basic strength of the aromatic amine increases.

e.g. $CH_3-C_6H_4-NH_2 > C_6H_5-NH_2$

19. (a) Electron withdrawing group ($-NO_2$) on benzene ring decreases the basicity and electron donating group ($-CH_3$) on benzene ring increases the basicity of the compound. Increasing order of basic strength :

p-nitroaniline < aniline < *p*-toluidine

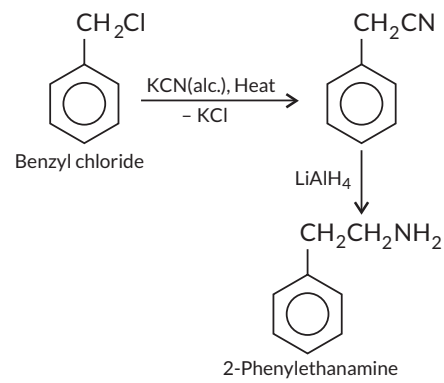
(b) Amines (like ammonia) are good nucleophiles. It is because alkyl group in an amine shows electron releasing effect. This increases the electron density on 'N' of amino group. This makes the amines very good nucleophiles.

$R \rightarrow \ddot{N}H_2$

(+*I* effect)

OR

(i)



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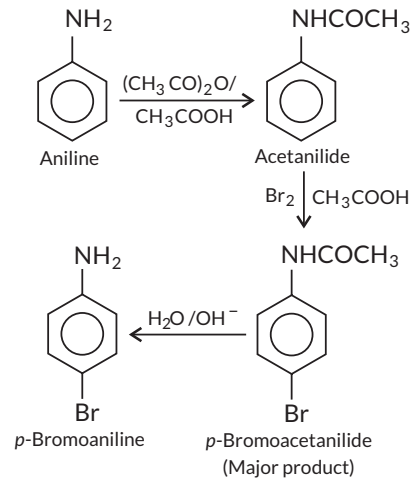

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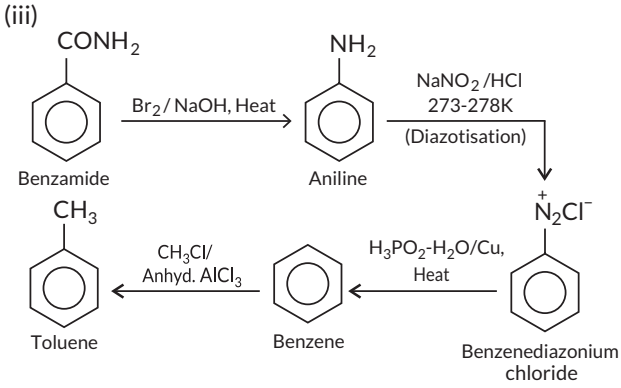


20. (i) In alkyl amines, a combination of +*I* effect of alkyl groups, steric factors and H-bonding factors determine the stability of ammonium cations in aqueous solution. All these factors are favourable for 2° amines and for smaller alkyl group, stability due to hydrogen bonding predominates over the stability due to +*I* effect. Consequently, we get the given K_b order :

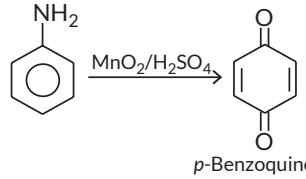
$Me_2NH > MeNH_2 > Me_3N$

(ii) Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

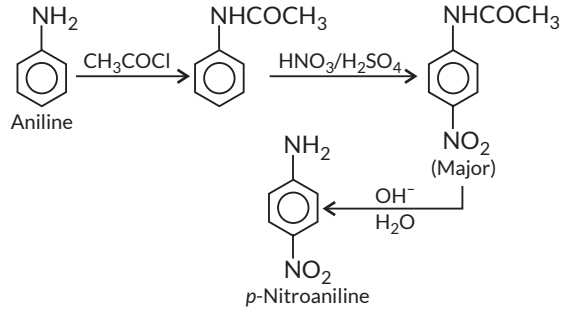
(iii) Tertiary amines do not undergo acylation reaction because they do not contain any H-atom on the nitrogen atom.

21. (a) Azo dye test is used to distinguish between cyclohexylamine and aniline.

(b)

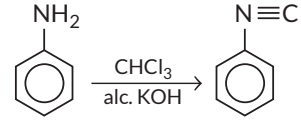


(c)



OR

Aniline gives phenyl isocyanide in carbylamine reaction.



22. (i) (a) $CH_3Br \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2}$

$CH_3CH_2OH \xleftarrow[273\ K]{HNO_2} \underset{(C)}{CH_3CH_2OH}$

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2 + KOH} \underset{(B)}{CH_3NH_2} \xrightarrow{CHCl_3 + NaOH} \underset{(C)}{CH_3NC}$

(ii) (a) Amides on reduction with $LiAlH_4$ or by reaction with Br_2 in presence of alkali give amines.

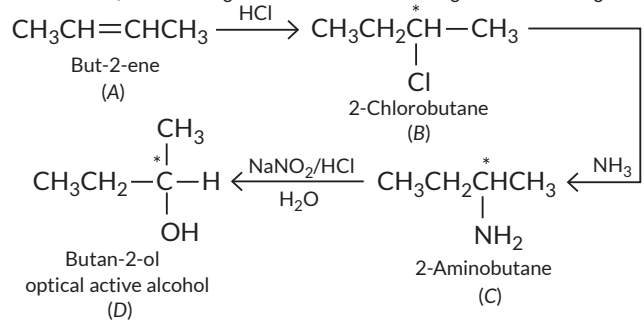
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2 + \bar{O}H} R-NH_2$$

(b) During acylation reaction HCl acid is formed. In order to remove HCl and shift the equilibrium to the right hand side a stronger base like pyridine is added.

$$R-NH_2 + R'COCl \xrightarrow{Pyridine} R-NHCOR' + HCl$$

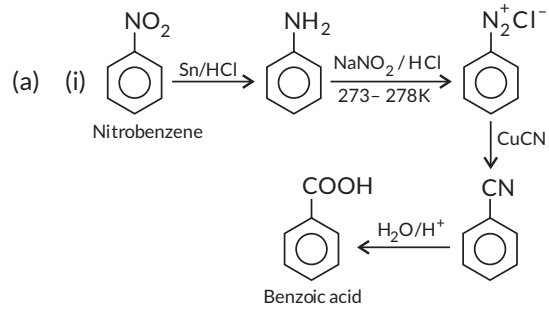
23. Since *A* undergoes ozonolysis it means it is an alkene. *C* gives diazonium salt that liberates N_2 and optically active alcohol. It shows *C* is an aliphatic amine. Product of ozonolysis is CH_3CHO hence *A* is $CH_3CH{=}CHCH_3$.



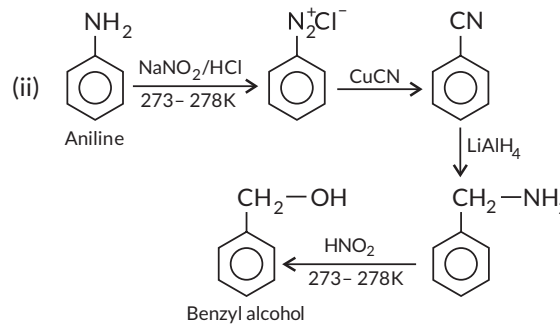
$$\underset{(A)}{CH_3CH{=}CHCH_3} \xrightarrow[Zn + H_2O]{O_3} 2\underset{\text{Acetaldehyde}}{CH_3CHO}$$

OR

(a) (i)



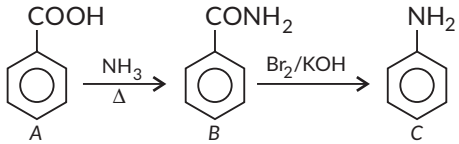
(ii)



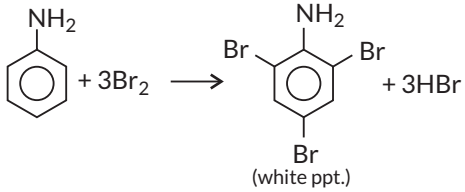
(b) (i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5CN$ (Benzonitrile, *(A)*) $\xrightarrow{H_2O/H^+} C_6H_5COOH$ (Benzoic acid, *(B)*) $\xrightarrow[\Delta]{NH_3} C_6H_5CONH_2$ (Benzamide, *(C)*)

(ii) $C_6H_5NO_2 \xrightarrow{Sn + HCl} C_6H_5NH_2$ (*A*) $\xrightarrow[273\ K]{NaNO_2 + HCl} C_6H_5N_2^+Cl^-$ (*B*) $\xrightarrow[\Delta]{H_2O} C_6H_5OH$ (*C*)

24. (a) Formula of the compound '*C*' indicates it is an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound '*B*' so compound '*B*' can be an amide. As '*B*' is obtained from compound '*A*' by reaction with ammonia followed by heating so, compound '*A*' could be an acid. Formula of compound '*C*' shows it to be aniline, then '*B*' is benzamide and compound '*A*' is benzoic acid. The sequence of reactions can be written as follows:



(b) (i) Aniline gives white or brown precipitate with bromine water.



Ethylamine does not react with bromine water.

(ii) When heated with an alcoholic solution of KOH and $CHCl_3$, ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

25. (i) (a) $CH_3-\underset{(X)}{\underset{|}{CH}}(NH_2)-\overset{*}{CH}-CH_3 \xrightarrow{NaNO_2/HCl}$

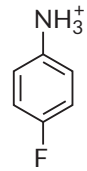
$CH_3-\underset{|}{\underset{OH}{CH}}-CH_2-CH_3 + N_2\uparrow + NaCl + H_2O$

Y (rearranged product)

$CH_3-\underset{|}{\underset{NH_2}{\overset{*}{CH}}}-CH_3 \xrightarrow[-N_2]{NaNO_2/HCl} CH_3-\underset{|}{\underset{H}{C}}-\overset{+}{CH}-CH_3$ (*X*)

$\xrightarrow{1,2\text{-}H^- \text{shift}} CH_3-\underset{+}{C}-CH_2-CH_3 \xrightarrow{H_2O} CH_3-\underset{|}{\underset{OH}{C}}-CH_2-CH_3$ (*Y*)

optically inactive

(b)  is more acidic due to the strong electron withdrawing power (–*I* effect) of fluorine.

(ii) $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow CH_2=\overset{+}{N}H_2$, $CH_3CH_2\ddot{N}H_2$

Acetamide Ethanamine

In acetamide, lone pair on nitrogen atom is involved in resonance and hence is not free for donation as in the case of ethanamine.

CHAPTER

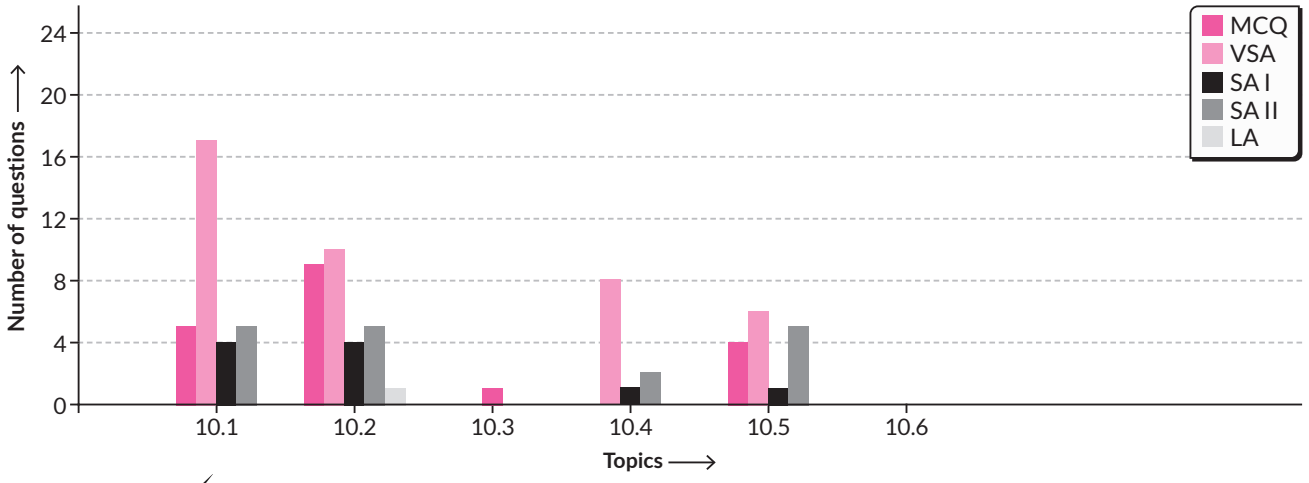
10

Biomolecules

TOPICS

10.1 Carbohydrates
10.2 Proteins
10.3 Enzymes
10.4 Vitamins
10.5 Nucleic Acids
10.6 Hormones

Analysis of Last 10 Years' CBSE Board Questions (2023-2014)



Weightage Xtract

- Topic 10.1 and 10.2 are highly scoring topics.
- Maximum total weightage is of Topic 10.1 *Carbohydrates.*
- Maximum VSA type questions were asked from Topic 10.1 *Carbohydrates.*
- Maximum SA I and SA II type questions were asked from Topic 10.1 *Carbohydrates* and Topic 10.2 *Proteins* respectively.

QUICK RECAP

CARBOHYDRATES

- **General formula :** $C_x(H_2O)_y$
- **Sugars or saccharides :** They are optically active polyhydroxy aldehydes or ketones.
- **Classification :** Carbohydrates are classified as either reducing or non-reducing sugars :

Carbohydrates

Reducing sugars

- Free aldehydic or ketonic group.
- Reduce Fehling's solution and Tollens' reagent
- *e.g.*, maltose and lactose

Non-reducing sugars

- Do not have free aldehydic or ketonic group.
- Do not reduce Fehling's solution and Tollens' reagent.
- *e.g.*, sucrose.

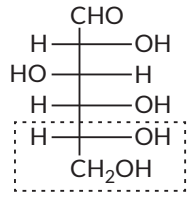
- On the basis of their behaviour towards hydrolysis :

Carbohydrates

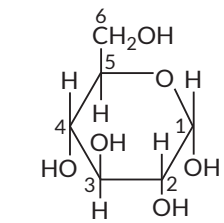
Monosaccharides	Oligosaccharides	Polysaccharides
Cannot be hydrolysed further. $(CH_2O)_n$, where, n = 3-7 *e.g.*, glucose, fructose, ribose, etc.	Yield 2-10 monosaccharides on hydrolysis. $(C_6H_{10}O_5)_n$, where n = 2-10 *e.g.*, sucrose, maltose etc.	Yield large number of monosaccharides on hydrolysis. $(C_6H_{10}O_5)_n$, where n, = 100-3000 *e.g.*, starch, cellulose, etc.

Monosaccharides :

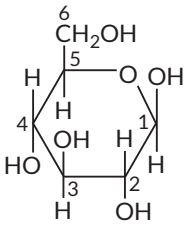
- **Glucose ($C_6H_{12}O_6$) :** Glucose is an aldohexose as it contains six carbon atoms with an aldehydic group.
  - **Structure :**



Fischer projection of *D*-(+)-Glucose



α-*D*-(+)-Glucopyranose



β-*D*-(+)-Glucopyranose

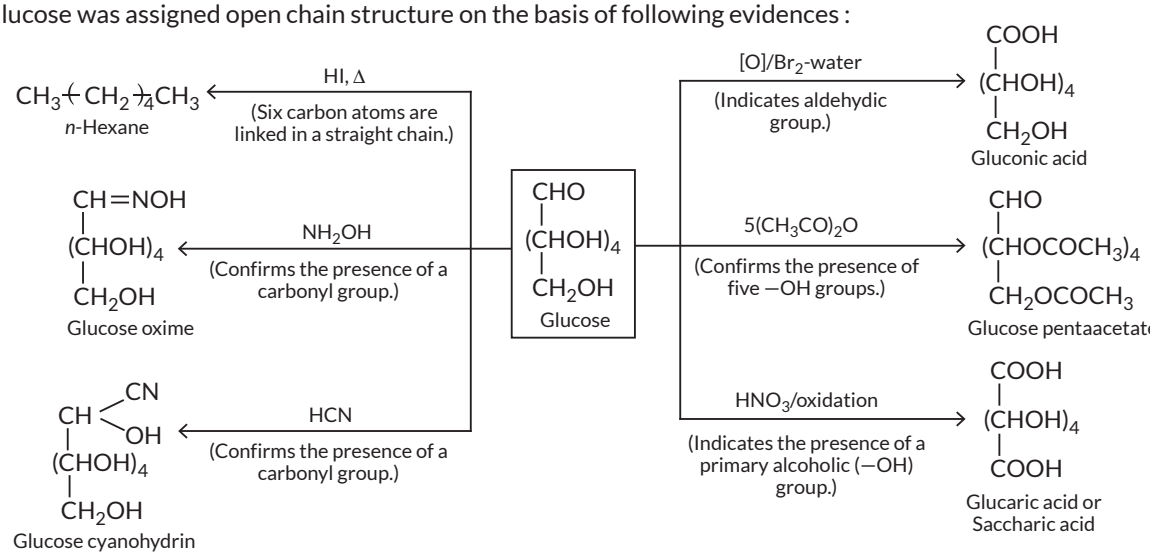
(Haworth Structures)

  - **Preparation :**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$
Sucrose — (Laboratory method)

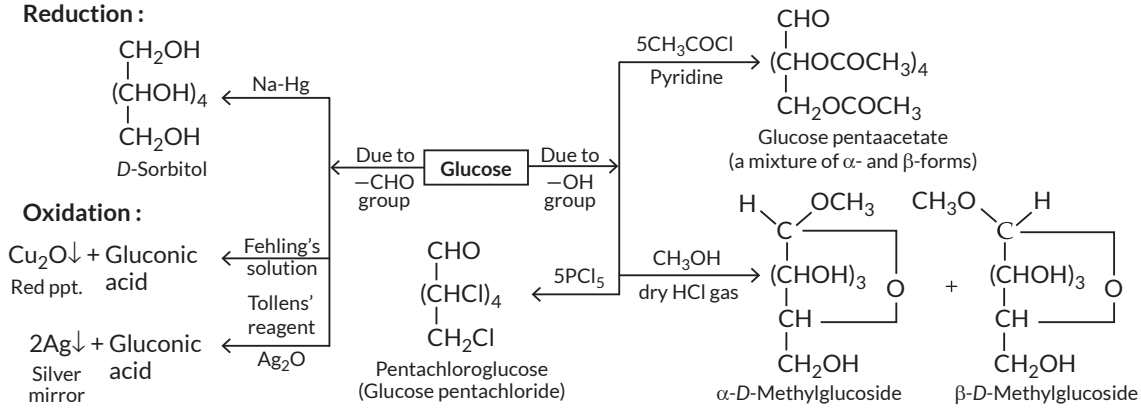
$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393\,K,\,2\text{-}3\,atm]{H^+/\Delta} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$
Starch or Cellulose — (Commercial method)

  - Glucose was assigned open chain structure on the basis of following evidences :

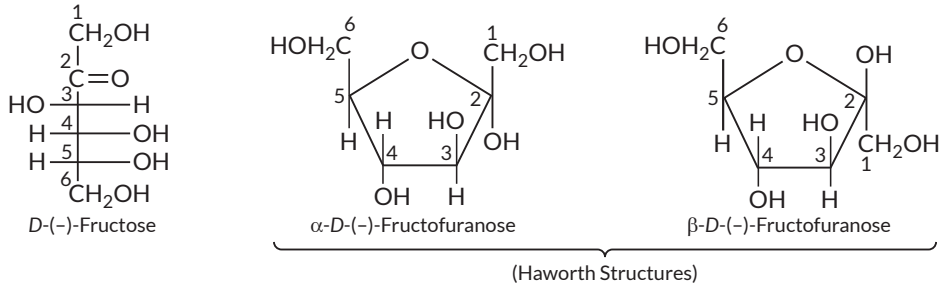


  - **Chemical reactions :**

Reduction :



- **Fructose ($C_6H_{12}O_6$) :** A ketohexose as it contains six carbon atoms with a ketonic group.
  - **Structure :**



- **Mutarotation :** The change in specific rotation of an optically active compound with time to an equilibrium value is called *mutarotation*.

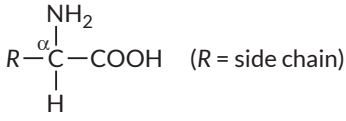
$$\underset{[\alpha]_D = +112^\circ}{\alpha\text{-}D\text{-Glucose}} \rightleftharpoons \underset{[\alpha]_D = +52.7^\circ}{\text{Equilibrium mixture}} \rightleftharpoons \underset{[\alpha]_D = +19^\circ}{\beta\text{-}D\text{-Glucose}}$$

Disaccharides and Polysaccharides

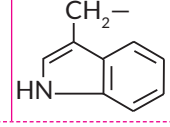
Carbohydrate	Hydrolysis products	Linkage	Reducing property
Sucrose (Disaccharide)	α-*D*-Glucose and β-*D*-Fructose	C-1 (Glucose) and C-2(Fructose)	Non-reducing
Maltose (Disaccharide)	α-*D*-Glucose	C-1 (Glucose) and C-4 (Glucose)	Reducing
Lactose (Disaccharide)	β-*D*-Galactose and β-*D*-Glucose	C-1 (Galactose) and C-4 (Glucose)	Reducing
Starch (Polysaccharide)	Amylose and Amylopectin	Amylose (C-1 and C-4 glycosidic linkage betweeen α-*D*-Glucose) Amylopectin (C-1 and C-4 linkage between α-*D*-Glucose and branching occurs by C-1 and C-6 linkage)	Non-reducing
Cellulose (Polysaccharide)	β-*D*-Glucose	C-1(Glucose) and C-4(Glucose)	Non-reducing
Glycogen (Polysaccharide)	α-*D*-Glucose	C-1 (Glucose) and C-4(Glucose)	Non-reducing

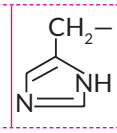
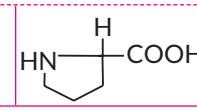
PROTEINS

Proteins : They are the biomolecules of the living system made up of nitrogenous organic compounds by condensation polymerisation of α-amino acids.



There are about 20 amino acids which make up the bioproteins. Out of these 10 amino acids **(non-essential)** are synthesised by our bodies and rest are essential in the diet **(essential amino acids)** and supplied to our bodies by food which we take because they cannot be synthesised in the body.

	Name of amino acid	Structure of *R*	Three letter symbol
1	Glycine	–H	Gly
2	Alanine	$-CH_3$	Ala
3	Valine*	$-CH(CH_3)_2$	Val
4	Leucine*	$-CH_2CH(CH_3)_2$	Leu
5	Isoleucine*	$-CH(CH_3)CH_2CH_3$	Ile
6	Arginine*	$-(CH_2)_3NH-C(=NH)-NH_2$	Arg
7	Lysine*	$-(CH_2)_4NH_2$	Lys
8	Glutamic acid	$-CH_2CH_2COOH$	Glu
9	Aspartic acid	$-CH_2COOH$	Asp
10	Glutamine	$-CH_2CH_2CONH_2$	Gln
11	Asparagine	$-CH_2CONH_2$	Asn
12	Threonine*	$-CHOH.CH_3$	Thr
13	Serine	$-CH_2OH$	Ser
14	Cysteine	$-CH_2SH$	Cys
15	Methionine*	$-CH_2CH_2SCH_3$	Met
16	Phenylalanine*	$-CH_2C_6H_5$	Phe
17	Tyrosine	$-CH_2C_6H_4OH(p)$	Tyr
18	Tryptophan*		Trp

19	Histidine*		His
20	Proline		Pro

*Essential amino acids

Classification of Amino Acids :

Classification of amino acids

Depending upon the relative number of amino ($-NH_2$) and carboxyl ($-COOH$) groups

Neutral
No. of $-COOH$ groups = No. of $-NH_2$ groups, *e.g.*, Glycine, Alanine, Valine

Acidic
No. of $-COOH$ groups > No. of $-NH_2$ groups, *e.g.*, Aspartic acid, Asparagine, Glutamic acid

Basic
No. of $-NH_2$ groups > No. of $-COOH$ groups, *e.g.*, Lysine, Arginine, Histidine

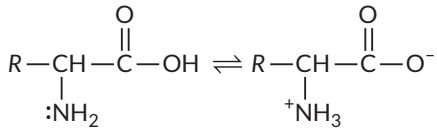
On the basis of their synthesis

Essential amino acids
Cannot be synthesised in the body and must be obtained through diet, *e.g.*, valine, leucine, lysine, isoleucine, argininine, etc.

Non-essential amino acids
Can be synthesised in the body.
e.g., glycine, alanine, glutamic acid, aspartic acid, etc.

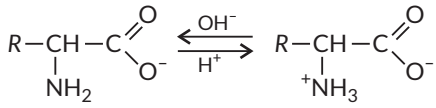
Properties :

- In aqueous solution, the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as *zwitter ion*. This is overall neutral but contains both positive and negative charges.

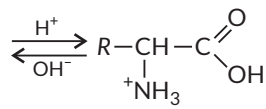


α-Amino acid Zwitter ion

- Since, these form salts with acids as well as with bases, their chemical reactions are similar to primary amines and carboxylic acids.

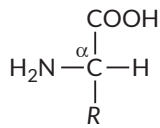


(In alkaline solution) (Neutral form)



(In acidic solution)

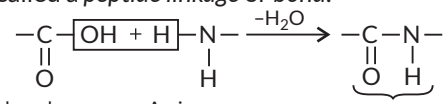
- **Isoelectric point :** The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, +ve and –ve charge is equal and it does not migrate to either electrode, is called *isoelectric point*. The amino acids have least solubility in water at isoelectric point which helps in their separation.
- Except glycine, all other naturally occurring α-amino acids are optically active because they contain chiral, asymmetric carbon atom.
- They exist in both *D*- and *L*-forms. Most naturally occurring α-amino acids have *L*-configuration.



L-Amino acid

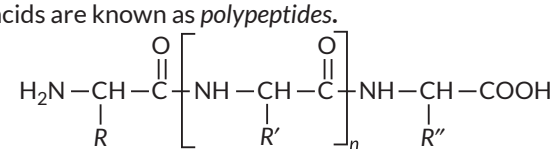
Peptides and their classification :

- **Peptide bond :** The bond formed between two amino acids by the elimination of a water molecule is called a *peptide linkage* or *bond*.



Carboxyl group of one amino acid Amino group of other amino acid Peptide bond

- The products formed by the linking of amino acids by peptide linkage are known as *peptides*.
- Peptides are further divided into *di*, *tri*, *tetra* depending upon the number of amino acids combined.
- **Oligopeptide :** It contains anywhere between 2-10 amino acids.
- **Polypeptides :** Structures with more than ten amino acids are known as *polypeptides*.



N-terminal amino acid C-terminal amino acid

where, *R*, *R′*, *R″* may be same or different.

- A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u is called a *protein*.

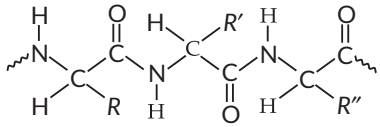
Classification of proteins : On the basis of molecular structure, proteins are classified as :

Fibrous proteins
In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin and myosin.

Globular proteins
Globular proteins result when the polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, *e.g.*, insulin and albumins.

Structure of proteins:

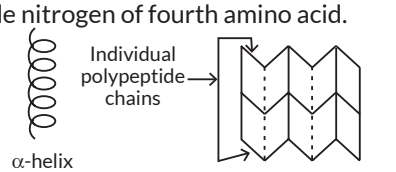
- **Primary structure :** It refers to the number and linear sequence of amino acids held together by peptide bonds.



Primary structure

- **Secondary structure:** It is due to folding or coiling of the peptide chain. It is mainly of two types :

– **α-Helix :** These coils are stabilized by hydrogen bonds between carbonyl oxygen of first amino acid to amide nitrogen of fourth amino acid.



α-helix
e.g., myosin (nucleus), keratin (hair) etc.

β-pleated sheet
e.g., silk protein (fibroin)

– **β-Pleated sheet structure :** β-Pleated sheet structure is formed when hydrogen bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains. The bonding in β-pleated sheet structure is intermolecular H-bonding. The structure is not planar but is slightly pleated. Silk fibroin is rich in β-pleated sheets.

- **Tertiary structure :** It represents overall folding of the polypeptide chains *i.e.*, further folding of the secondary structure and the bonds responsible for such interaction are hydrophobic interactions, hydrogen bonds, ionic interactions, van der Waals' forces and disulphide bonds.
- **Quaternary structure :** This is the spatial arrangement of the subunits (two or more polypeptide chains) with respect to each other.

Denaturation of proteins :

- When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix gets uncoiled and protein loses its biological activity. This is called *denaturation of protein*.
- The denaturation causes change in secondary and tertiary structures but primary structure remains intact, *e.g.*, coagulation of egg white on boiling, curdling of milk, formation of cheese when an acid is added to milk.

ENZYMES

The enzymes are biocatalysts produced by living cells which catalyse biochemical reactions in living organisms. Chemically, enzymes are naturally occurring simple or conjugated proteins. Some enzymes may be non-proteins also.

HORMONES

Hormones : They are the molecules that act as intercellular messengers and are poured directly in the blood stream by endocrine glands.

Types of hormones :

- **Steroids :** Estrogens and androgens
- **Polypeptides :** Insulin and endorphins
- **Amino acid derivatives :** Epinephrine and norepinephrine.

VITAMINS

Vitamins: These are complex organic molecules which cannot be produced by the body and must be supplied in small amounts in diet to carry out essential metabolic reactions which are required for normal growth and maintenance of the body.

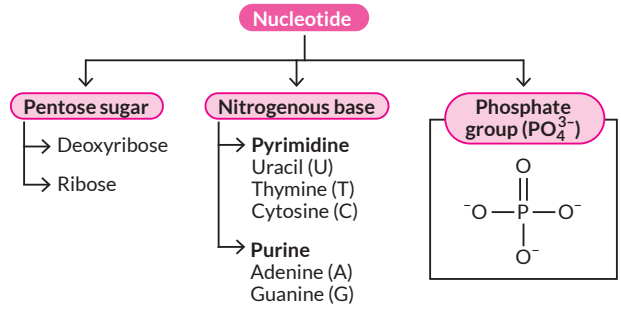
Classification :

- **Water soluble vitamins :** Soluble in water. Must be supplied regularly in diet as they are regularly excreted in urine (except vitamin B_{12}), *e.g.*, Vitamin–B_1, B_2, B_6, B_{12} and C.

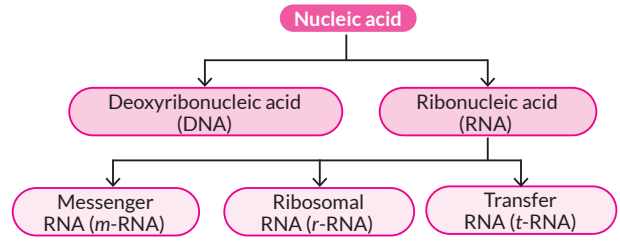
  Fat soluble vitamins : Soluble in fat and oils. Stored in liver and adipose tissues, *e.g.*, Vitamin – A, D, E and K.

NUCLEIC ACIDS

Nucleic acids are the *polymers of nucleotides* present in nucleus of all living cells and play an important role in transmission of the hereditary characteristics and biosynthesis of proteins.



Types of nucleic acids :



Chargaff's rule : Amount of purine bases is always equal to that of pyrimidine bases. Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand. Adenine (A) pairs with thymine (T) through two H-bonds (A═T) and guanine (G) pairs with cytosine (C) through three H-bonds (G≡C). In case of RNA, adenine (A) pairs with uracil (U), (A═U).

Replication : It is the process by which a single DNA molecule produces two identical copies of itself.

Protein synthesis : It occurs in two steps :

- **Transcription :** It is the process of synthesis of RNA.
- **Translation :** The synthesis of proteins occur in the cytoplasm of the cell. The *m*-RNA directs protein synthesis with the help of *r*-RNA and *t*-RNA.

BIOMOLECULES

Carbohydrates (saccharides)

Optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.

Classification

On the basis of their behaviour on hydrolysis.

Monosaccharides : cannot be hydrolysed further. On the basis of number of carbon atoms and functional group present.

Types

- **Aldoses** — Contain aldehyde group (–CHO) *e.g.* glucose, arabinose, ribose, etc.
- **Ketoses** — Contain keto group (> C = O) *e.g.* ribulose, fructose, etc.

Oligosaccharides : Yields 2-10 monosaccharide units on hydrolysis classification:

(on the basis of number of monosaccharide units given)

- **Disaccharides**
- **Trisaccharides** — *e.g.*, raffinose
- **Tetrasaccharides** — *e.g.*, stachyrose

Sucrose (Non-reducing) : *D* – (+) – glucose and *D* – (–) – fructose held by **glycosidic linkage** between C1 of α-glucose and C2 of β-fructose. On hydrolysis it changes from dextro (+) to laevo (–) → **Invert sugar**.

Maltose (Reducing): Two α – *D* – glucose units in which C1 of one glucose linked to C4 of another glucose unit.

Lactose (Reducing) (Milk sugar): β – *D* – glucose and β – *D* – galactose have glycosidic linkage between C1 of galactose and C4 of glucose.

Polysaccharides : Yield a large number of monosaccharide units. *e.g.*, starch, cellulose, glycogen, etc.

Starch : Polymer of α-glucose, have 2 components – Amylose (15-20%) (water soluble) → unbranched chain polymer and amylopectin (80-85%) (water insoluble) → branched chain polymer.

Cellulose : In plants cell wall, straight chain, composed of β-*D*-glucose units joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

Glycogen : In animals brain, liver and muscles. Similar to amylopectin.

Importance

Starch – storage in plants.
Glycogen – in animals.
Cellulose – cell wall of bacteria and plants
aldopentoses *viz*. *D*-ribose and 2-deoxy-*D*-ribose - present in nucleic acids.

Proteins

are the polymers of α-amino acids connected to each other by Peptide Bond or Peptide Linkage.

↓ Hydrolysis

Peptides

↓ Hydrolysis

α-amino acids.

$$(R-\underset{\displaystyle H}{\overset{\displaystyle NH_2}{\underset{|}{\overset{|}{C}}}}-COOH)$$

- **Essential amino acids:** Which cannot be synthesised in the body and must be obtained through diet.
- **Non-essential amino acids :** (10) (dispensable) can be synthesized by body.

Classification

Based on molecular structure

- **Fibrous :** Thread like *e.g.*, keratin, collagen, myosin, etc.
- **Globular :** Spheroidal *e.g.*, insulin, Hb, antibodies, albumin, etc.

Structure

- **Primary :** Sequence of α-amino acids.
- **Secondary :** Shape due to H-bonding.
- **Tertiary :** Overall folding of the polypeptide chains (secondary structure).
- **Quaternary :** Spatial arrangement of subunits w.r.t. each other.

Denaturation

On heating or treatment with mineral acid, protein undergo coagulation *i.e.*, native shape of the protein is destroyed and biological activity is lost (2° and 3° structures destroyed, 1° remains intact)

Nucleic Acids

(Pentose sugar + base + phosphoric acid)

- **DNA** — Sugar is β-*D*-2-deoxyribose. 4 bases are : Adenine (A), Guanine (G), Cytosine (C), Thymine (T).
- **RNA** — Sugar is β-*D*-ribose. 3 bases are same + fourth one is Uracil (U) instead of Thymine (T).

BRAIN MAP

Previous Years' CBSE Board Questions

10.1 Carbohydrates

MCQ

1. Which of the following is a non-reducing sugar?
   (a) Sucrose (b) Maltose
   (c) Glucose (d) Lactose *(2023)*

2. The glycosidic linkage involved in linking the glucose units in amylose part of starch is
   (a) $C_1 - C_6$ α linkage (b) $C_1 - C_6$ β linkage
   (c) $C_1 - C_4$ α linkage (d) $C_1 - C_4$ β linkage
   (2023)

3. Which of the following sugar is known as dextrose?
   (a) Glucose (b) Fructose
   (c) Ribose (d) Sucrose
   (Term I, 2021-22)

4. α–*D*(+) glucose and β–*D*(+) glucose are
   (a) geometrical isomers (b) enantiomers
   (c) anomers (d) optical isomers.
   (2020) Ap

5. **Assertion (A) :** Sucrose is a non-reducing sugar.
   Reason (R) : Sucrose has glycosidic linkage.
   (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
   (d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)* An

VSA (1 mark)

6. Name the disaccharide which on hydrolysis gives two molecules of glucose. *(One word, 2020)*
7. Write the name of linkage joining two monosaccharides. *(One word, 2020)*
8. What is the basic structural difference between glucose and fructose? *(Delhi 2019)* R
9. Write the structural difference between starch and cellulose. *(AI 2019, 2016)*
10. Write the products obtained after hydrolysis of lactose. *(Delhi 2019)*

    OR

    Write the name of two monosaccharides obtained on hydrolysis of lactose sugar. *(Delhi 2016)*
11. Name a carbohydrate present in liver, muscles and brain. *(2019C)*
12. What are the hydrolysis products of sucrose ? *(2019C)*
13. Define the following with an example :
    Polysaccharides *(1/3, 2018)*

    OR

    Define the following term : Polysaccharides
    (Foreign 2014)
14. Write the product when *D*-glucose reacts with conc. HNO_3. *(1/3, 2018)*
15. Which one of the following is a disaccharide : Starch, Maltose, Fructose, Glucose? *(Delhi 2015)* Ev
16. Write the product obtained when *D*-glucose reacts with H_2N-OH. *(AI 2015)*
17. Which one of the following is a monosaccharide : starch, maltose, fructose, cellulose *(Foreign 2015)* U
18. Which of the two components of starch is water soluble? *(Delhi 2014)*
19. Write the product formed on reaction of *D*-glucose with Br_2 water. *(Delhi 2014)*
20. Write the product formed when glucose is treated with HI. *(Delhi 2014)* Ap
21. Define the following term : Anomers
    (AI 2014, Foreign 2014)
22. Define the following term : Invert sugar
    (Foreign 2014)

SA I (2 marks)

23. Give the reaction of heating glucose with hydroxylamine. Presence of which group is confirmed by this reaction? *(2023)*
24. Define the following terms :
    (i) Oligosaccharides
    (ii) Invert sugar *(2020)* R
25. Write the reactions showing the presence of following in the open structure of glucose :
    (i) an aldehyde group
    (ii) a primary alcohol. *(2020)*
26. Enumerate the reactions of glucose which cannot be explained by its open chain structures. *(Delhi 2014C)*

SA II (3 marks)

27. (a) What are the hydrolysis products of (i) Lactose, (ii) Maltose?
    (b) Give the basic structural difference between starch and cellulose. *(2023)*
28. Write the reaction of glucose with
    (i) HCN (ii) Br_2 (iii) HI *(2021 C)*
29. Write chemical reactions to show that open structure of *D*-glucose contains the following :
    (i) Straight chain
    (ii) Five alcohol groups
    (iii) Aldehyde as carbonyl group. *(Delhi 2019)* U
30. What happens when *D*-glucose is treated with the following reagents?
    (a) Br_2 water (b) HCN
    (c) $(CH_3CO)_2O$ *(AI 2019)*

31. Define the following terms :
(i) Glycosidic linkage (ii) Invert sugar
(iii) Oligosaccharides *(AI 2014)*

10.2 Proteins

MCQ

32. β-pleated sheet structure in proteins refers to
(a) primary structure (b) secondary structure
(c) tertiary structure (d) quaternary structure. *(2023)*

33. An α-helix is a structural feature of
(a) sucrose (b) starch
(c) polypeptides (d) nucleotides. *(2023)*

34. Complete the following analogy :
Curdling of milk : A :: α-helix : B
(a) A : Primary structure , B : Secondary structure
(b) A : Denatured protein, B : Primary structure
(c) A : Secondary structure, B : Denatured protein
(d) A : Denatured protein, B : Secondary structure
(Term I, 2021-22) An

35. Amino acids which cannot be synthesized in the body and must be obtained through diet are known as
(a) acidic amino acids
(b) essential amino acids
(c) basic amino acids
(d) non-essential amino acids. *(Term I, 2021-22)*

36. The helix structure of proteins is stabilised by:
(a) peptide bond (b) hydrogen bond
(c) disulphide bond (d) van der Waals' forces *(2021C)*

37. Peptide linkage is present in
(a) carbohydrates (b) vitamins
(c) protein (d) rubber. *(2020)* U

38. Amino acids are
(a) acidic (b) basic
(c) amphoteric (d) neutral. *(2020)* R

39. **Assertion (A) :** Albumin is a globular protein.
Reason (R) : Polypeptide chain coils around to give a straight chain.
(a) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the assertion (A).
(b) Both assertion (A) and reason (R) are correct statements, but reason (R) is not the correct explanation of the assertion (A).
(c) Assertion (A) is correct, but reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but reason (R) is correct statement. *(2020)*

40. An α-helix is a structural feature of
(a) sucrose (b) polypeptides
(c) nucleotides (d) starch. *(2020)*

VSA (1 mark)

41. What is the difference between a glycosidic linkage and a peptide linkage ? *(2019)* U

42. Define the following terms with a suitable example of each :
(a) Anomers (b) Essential amino acids
(c) Denaturation of protein *(2019)*

43. What is the difference between fibrous protein and globular protein? *(1/3, AI 2017C, Delhi 2015)*

44. Give one example each for fibrous protein and globular protein. *(AI 2016, Delhi 2014)*

45. Amino acids show amphoteric behaviour. Why?
(AI 2015) An

46. What is the difference between acidic amino acids and basic amino acids? *(Foreign 2015)*

47. What type of linkage is responsible for the formation of proteins? *(Delhi, Foreign 2014)*

48. Define the following term :
Essential amino acids *(AI 2014)*

49. Define the following term :
Denaturation of proteins *(Foreign 2014)*

50. Define the following term :
Amino acids *(Foreign 2014)* R

SA I (2 marks)

51. Define denaturation of protein. What is the effect of denaturation on the structure of protein? *(2023)*

52. (a) Write chemical reaction to show that open structure of *D*-glucose contains the straight chain.
(b) What type of linkage is responsible for the formation of protein? *(2023)*

53. Define the following with an example of each :
(i) Denatured protein
(ii) Essential amino acids *(2/3, 2018)*

54. (a) Amino acids show amphoteric behaviour. Why?
(b) Write one difference between α-helix and β-pleated structures of proteins. *(2/3, 2018)*

SA II (3 marks)

55. (a) Write the product when *D*-glucose reacts with conc. HNO_3.
(b) Amino acids show amphoteric behaviour. Why?
(c) Write one difference between α-helix and β-pleated structure of protein. *(2023)*

56. Define proteins and classify them on the basis of their molecular shape. *(2020C)*

57. Differentiate between the following :
(i) Amylose and Amylopectin
(ii) Peptide linkage and Glycosidic linkage
(iii) Fibrous proteins and Globular proteins.
(Delhi 2019) Ev

58. Define the following terms as related to proteins :
(i) Peptide linkage (ii) Primary structure
(iii) Denaturation *(AI 2015, 2014)*

59. What are essential and non-essential amino acids? Give two examples of each. *(AI 2014C)*

Case Based (5 marks)

60. **Read the given passage and answer the questions number (i) to (v) that follow :** 1×5=5
Organic compounds containing amine as functional group are present in a vivid variety of compounds, namely amino acids, hormones, neurotransmitters, DNA, alkaloids, dyes, etc. Drugs including nicotine, morphine, codeine and heroin, etc. which have physiological effects on humans also contain amino group in one form or another. Amines are basic because of the presence of lone pair of electrons on nitrogen. Addition of nitrogen into an organic framework leads to the formation of two families of molecules, namely amines and amides. As chemistry students, we must appreciate the versatility of nitrogen.
(i) What are amino acids ?
(ii) Why are amino acids amphoteric ?
(iii) Give one point of difference between acidic and basic amino acid.
(iv) What are essential amino acids ?
(v) Name the linkage formed when carboxyl end of one amino acid condenses with amino end of other amino acid. *(2020)*

10.3 Enzymes

VSA (1 mark)

61. Define the following term :
Enzymes *(Foreign 2014, AI 2014 C)*

10.4 Vitamins

VSA (1 mark)

62. Why vitamin C cannot be stored in our body? *(Delhi 2016)*
63. Write the name of vitamin whose deficiency causes bone deformities in children. *(Delhi 2015)*
64. Write the name of the vitamin whose deficiency causes bleeding of gums. *(Foreign 2015)*
65. Deficiency of which vitamin causes night-blindness? *(Delhi 2014)* R
66. Deficiency of which vitamin causes rickets? *(Delhi 2014)*
67. Deficiency of which vitamin causes scurvy? *(Delhi 2014)*
68. Define the following term : Vitamins *(Foreign 2014)* R
69. Why are vitamin *A* and vitamin *C* essential for us? *(Delhi 2014C)*

SA I (2 marks)

70. Define vitamins and classify them on the basis of their solubility. *(2020C)* R

SA II (3 marks)

71. (a) What are the products of hydrolysis of maltose ?
(b) What type of bonding provides stability to α-helix structure of protein ?
(c) Name the vitamin whose deficiency causes pernicious anaemia. *(2019)*
72. How are vitamins classified? Name the vitamin responsible for the coagulation of blood. *(Delhi 2015C)*

10.5 Nucleic Acids

MCQ

73. **Assertion :** The backbone of DNA and RNA molecules is a chain consisting of heterocyclic base, pentose sugar and phosphate group.
Reason : Nucleotides and nucleosides mainly differ from each other in presence of phosphate group.
(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A)
(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A)
(c) Assertion (A) is true, but Reason (R) is false.
(d) Assertion (A) is false, but Reason (R) is true. *(2023)*
74. The base which is present in DNA but not in RNA, is
(a) cytosine (b) guanine (c) adenine (d) thymine. *(Term I, 2021-22)* R
75. Nucleic acids are polymer of
(a) amino acids (b) nucleosides
(c) nucleotides (d) glucose. *(Term I, 2021-22, 2021C)*
76. Nucleosides are composed of
(a) a pentose sugar and phosphoric acid
(b) a nitrogenous base and phosphoric acid
(c) a nitrogenous base and a pentose sugar
(d) a nitrogenous base, a pentose sugar and phosphoric acid. *(Term I, 2021-22)* R

VSA (1 mark)

77. Name the unit formed by the attachment of a base to 1′ position of sugar. *(2020C)*
78. Write the products obtained after hydrolysis of DNA. *(2019)*
79. What is difference between a nucleoside and nucleotide? *(2019, Delhi 2016, 2014C)*
80. What type of linkage is present in nucleic acids? *(AI 2016)* U
81. Name of the base that is found in nucleotide of RNA only. *(Delhi 2014)*
82. Define the following term :
Nucleoside *(Foreign 2014)* R

SA I (2 marks)

83. Write two differences between DNA and RNA. *(2019)*

SA II (3 marks)

84. Give reasons for any 3 of the following observations:
(a) Penta-acetate of glucose does not react with hydroxylamine.
(b) Amino acids behave like salts.
(c) Water soluble vitamins must be taken regularly in diet.
(d) The two strands in DNA are complimentary to each other. *(2023)*

85. Differentiate the following
(i) Fibrous protein and Globular protein
(ii) Essential amino acids and Non-essential amino acids
(iii) DNA and RNA *(2021C)* U

86. Define the following terms :
(a) Invert sugar (b) Native protein
(c) Nucleotide *(2019)*

87. Give the plausible explanation for the following :
(a) Glucose doesn't give 2,4-DNP test.
(b) The two strands in DNA are not identical but are complementary.
(c) Starch and cellulose both contain glucose unit as monomers yet they are structurally different. *(2020)*

88. Differentiate between following :
(i) Amylose and Amylopectin
(ii) Globular protein and Fibrous protein
(iii) Nucleotide and Nucleoside *(2020)* Ap

CBSE Sample Questions

10.1 Carbohydrates

MCQ

1. Which one of the following reactions is not explained by the open chain structure of glucose?
(a) Formation of pentaacetate of glucose with acetic anhydride
(b) Formation of addition product with 2,4 DNP reagent
(c) Silver mirror formation with Tollen's reagent
(d) Existence of alpha and beta forms of glucose
(Term I, 2021-22) U

2. Which of the following is a polysaccharide?
(a) Glucose (b) Maltose
(c) Glycogen (d) Lactose
(Term I, 2021-22)

3. Which one of the following statements is correct about sucrose?
(a) It can reduce Tollen's reagent, however cannot reduce Fehling's reagent.
(b) It undergoes mutarotation like glucose and fructose.
(c) It undergoes inversion in the configuration on hydrolysis.
(d) It is laevorotatory in nature.
(Term I, 2021-22) R

4. In the following reaction,identify *A* and *B*.

$$C_6H_{12}O_6 \xrightarrow{\text{Acetic anhydride}} A$$
$$\downarrow \text{Conc. nitric acid}$$
$$B$$

(a) $A = COOH—(CH_2)_4—COOH$,
$B = OHC—(CHOCOCH_3)_4 — CH_2OCOCH_3$
(b) $A = COOH—(CH_2)_4—CHO$,
$B = OHC—(CHOCOCH_3)_4—CH_2OCOCH_3$
(c) $A = OHC—(CHOCOCH_3)_3—CH_2OCOCH_3$,
$B = COOH—(CH_2)_4—CHO$
(d) $A = OHC—(CHOCOCH_3)_4—CH_2OCOCH_3$,
$B = COOH—(CHOH)_4—COOH$ *(Term I, 2021-22)*

5. Dissacharides that are reducing in nature are
(a) sucrose and lactose
(b) sucrose and maltose
(c) lactose and maltose
(d) sucrose, lactose and maltose. *(2020-21)*

SA I (2 marks)

6. Account for the following:
(a) There are 5 -OH groups in glucose.
(b) Glucose is a reducing sugar.

OR

What happens when *D*-glucose is treated with the following reagents?
(a) Bromine water
(b) HNO_3 *(2022-23)*

10.2 Proteins

MCQ

7. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Proteins are found to have two different types of secondary structures *viz* alpha-helix and beta-pleated sheet structure.
Reason (R) : The secondary structure of proteins is stabilized by hydrogen bonding.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(2022-23)*

8. Which of the following statements is correct?
(a) Fibrous proteins are generally soluble in water.
(b) Albumin is an example of fibrous protein.
(c) In fibrous proteins, the structure is stabilised by hydrogen bonds and disulphide bonds.
(d) pH does not affect the primary structure of protein. *(Term I, 2021-22)* An

9. Curdling of milk is an example of
(a) breaking of peptide linkage
(b) hydrolysis of lactose
(c) breaking of protein into amino acids
(d) denaturation of protein. *(2020-21)*

SA II (3 marks)

10. Three amino acids are given below :
Alanine : $CH_3CH(COOH)(NH_2)$,

Aspartic acid : HOOC – $CH_2CH(COOH)(NH_2)$ and
Lysine : H_2N – $(CH_2)_4$ – $CH(COOH)(NH_2)$
(i) Make two tripeptides using these amino acids and mark the peptide linkage in both cases.
(ii) Represent alanine in the zwitter ionic form.
(2020-21) Cr

10.5 Nucleic Acids

MCQ

11. Match the following:

I		II	
(i)	Amino acids	(A)	Protein
(ii)	Thymine	(B)	Nucleic acid
(iii)	Insulin	(C)	DNA
(iv)	Phosphodiester linkage	(D)	Zwitter ion
(v)	Uracil		

Which of the following is the best matched options?
(a) (i)-A, (v)-D, (iii)-C, (iv)-B (b) (i)-D, (ii)-C, (iii)-A, (iv)-B
(c) (i)-D, (v)- D, (iii)-A, (iv)-B (d) (i)-A, (ii)-C, (iii)-D, (iv)-B
(Term I, 2021-22) An

12. **Assertion :** The two strands are complementary to each other.
Reason : The hydrogen bonds are formed between specific pairs of bases.
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement. *(2020-21)*

Case Based (5 marks)

13. **Strengthening the Foundation: Chargaff Formulates His "Rules"**
Many people believe that James Watson and Francis Crick discovered DNA in the 1950s. In reality, this is not the case. Rather, DNA was first identified in the late 1860s by Swiss chemist Friedrich Miescher. Then, in the decades following Miescher's discovery, other scientists-notably, Phoebus Levene and Erwin Chargaff carried out a series of research efforts that revealed additional details about the DNA molecule, including its primary chemical components and the ways in which they joined with one another. Without the scientific foundation provided by these pioneers, Watson and Crick may never have reached their groundbreaking conclusion of 1953: that the DNA molecule exists in the form of a three-dimensional double helix.
Chargaff, an Austrian biochemist, as his first step in this DNA research, set out to see whether there were any differences in DNA among different species. After developing a new paper chromatography method for separating and identifying small amounts of organic material, Chargaff reached two major conclusions:
(i) the nucleotide composition of DNA varies among species.
(ii) Almost all DNA, no matter what organism or tissue type it comes from maintains certain properties, even as its composition varies. In particular, the amount of adenine (A) is similar to the amount of thymine (T), and the amount of guanine (G) approximates the amount of cytosine (C). In other words, the total amount of purines (A + G) and the total amount of pyrimidines (C + T) are usually nearly equal. This conclusion is now known as "Chargaff's rule." Chargaff's rule is not obeyed in some viruses. These either have single- stranded DNA or RNA as their genetic material.

Answer the following questions:
(a) A segment of DNA has 100 adenine and 150 cytosine bases. What is the total number of nucleotides present in this segment of DNA?
(b) A sample of hair and blood was found at two sites. Scientists claim that the samples belong to same species. How did the scientists arrive at this conclusion?
(c) The sample of a virus was tested and it was found to contain 20% adenine, 20% thymine, 20 % guanine and the rest cytosine. Is the genetic material of this virus (a) DNA- double helix (b) DNA-single helix (c) RNA? What do you infer from this data?

OR

How can Chargaff's rule be used to infer that the genetic material of an organism is double- helix or single- helix? *(2022-23)*

Detailed SOLUTIONS

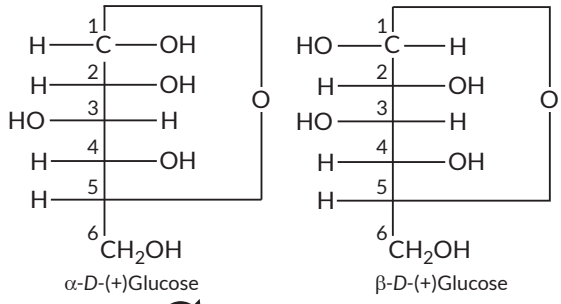
Previous Years' CBSE Board Questions

1. (a): Sucrose is a non-reducing sugar which on hydrolysis gives equimolar mixture of α-*D*(+)-glucose and β-*D*(–)-fructose. Since, the reducing groups of glucose and fructose are involved in a glycosidic bond formation (C1 of α-glucose and C2 of β-fructose), hence sucrose is a non-reducing sugar.

2. (c): Starch is main storage polysaccharide of plants. It is a polymer of α-*D*-glucose and consists of two components – Amylose and Amylopectin. Amylose is held by C_1 – C_4 α-glycosidic linkage while amylopectin is formed by α – C_1 – C_4 and α – C_1 – C_6 glycosidic linkage.

3. **(a):** Glucose is known as dextrose.

4. **(c):** The pair of stereoisomers which differ only in the configuration of the hydroxyl group at C_1 are called anomers.



Concept Applied

➲ Anomers differ in configuration at C-1 only.

5. **(a):** Sucrose is disaccharide and its two monosaccharides are held together by a glycosidic linkage. Since, the reducing groups of glucose and fructose are involved in glycosidic bond formation, therefore, sucrose is a non-reducing sugar.

6. Maltose

7. Glycosidic linkage

8. Glucose contains an aldehydic group while fructose contains a ketonic group.

9. The basic structural difference between starch and cellulose is of linkage between the glucose units.

In starch, there is α-*D*-glycosidic linkage. Both the components of starch-amylose and amylopectin are polymer of α-*D*-glucose. On the other hand, cellulose is a linear polymer of β-*D*-glucose in which C_1 of one glucose unit is connected to C_4 of the other through β-*D*-glycosidic linkage.

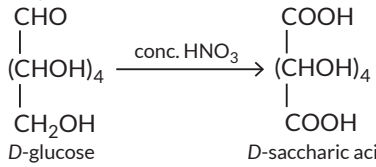
10. Lactose on hydrolysis gives β-*D*-glucose and β-*D*-galactose.

11. Carbohydrate is present in the form of glycogen in liver, muscles and brain.

12. Hydrolysis products of sucrose are glucose and fructose.

13. Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides, *e.g.*, cellulose.

14. On oxidation with nitric acid, *D*-glucose yields saccharic acid.

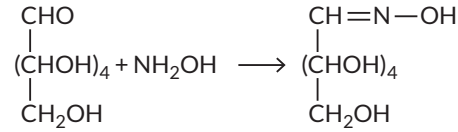


Answer Tips

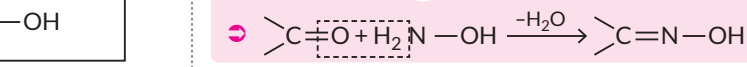
➲ Oxidation of *D*-glucose takes place in presence of nitric acid.

15. Maltose is a disaccharide as it consists of two α-*D*-glucose units.

16. *D*-Glucose reacts with $H_2N—OH$ to give glucose oxime.



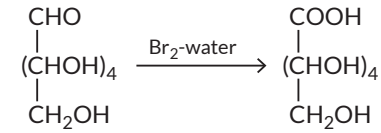
Concept Applied

➲ 

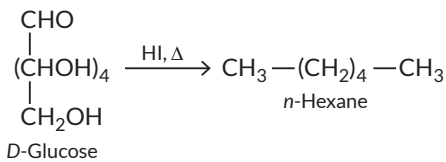
17. Fructose is a monosaccharide because it cannot be hydrolysed to simpler polyhydroxy aldehydes or ketones.

18. Amylose is water soluble and amylopectin is insoluble in water.

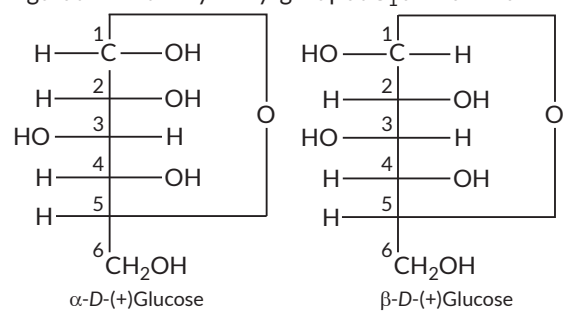
19. *D*-Glucose gets oxidised to carboxylic acid (gluconic acid) on reaction with bromine water.



20. On prolonged heating with HI, *D*-glucose forms *n*-hexane.

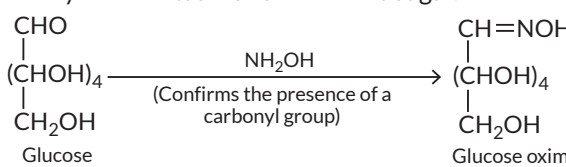


21. The pair of stereoisomers which differ only in the configuration of the hydroxyl group at C_1 are called anomers.



22. An equimolar mixture of glucose and fructose, obtained by hydrolysis of sucrose in presence of an acid or the enzyme invertase is called invert sugar.

23.

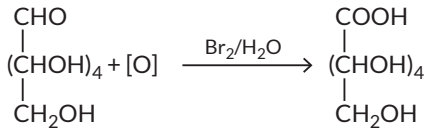


24. (i) These are the carbohydrates which on hydrolysis give 2-10 monosaccharides. For example, sucrose, lactose, maltose, etc.

(ii) An equimolar mixture of glucose and fructose, obtained by hydrolysis of sucrose in presence of an acid or the enzyme invertase is called invert sugar.

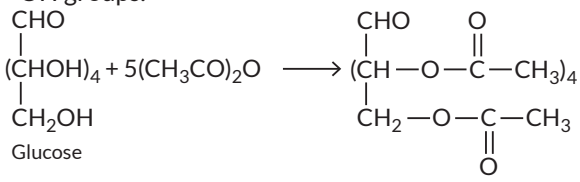
25. (i) Glucose on oxidation with a mild oxidising agent like bromine water gives gluconic acid containing

the same six carbon atoms as present in glucose. This indicates presence of aldehyde group.



Gluconic acid

(ii) On acetylation with acetic anhydride, glucose gives a pentaacetate. This confirms that glucose contains five –OH groups.

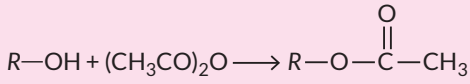


Glucose pentaacetate

$+ 5CH_3COOH$

Concept Applied

➲ —OH group reacts with acetic anhydride while aldehyde group does not react with anhydrides.



26. The following reactions of *D*-glucose cannot be explained on the basis of its open chain structure :

(i) *D*-Glucose does not react with sodium bisulphite ($NaHSO_3$).

(ii) It does not give 2, 4-DNP test and Schiff's test.

(iii) The pentaacetate of *D*-glucose does not react with hydroxylamine.

(iv) *D*-Glucose shows the phenomenon of mutarotation *i.e.*, when its aqueous solution is kept for sometime its optical activity changes.

(v) On reaction with 1 mole of methanol, it yields two monomethyl derivatives which are known as methyl α-*D*-glucoside and methyl-β-*D*-glucoside.

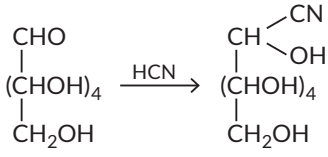
27. (a) (i) On hydrolysis lactose gives, β-*D*-glucose and β-*D*-galactose.

(ii) On hydrolysis maltose gives, α-*D*-glucose units only.

(b) The basic structural difference between starch and cellulose is of linkage between the glucose units.

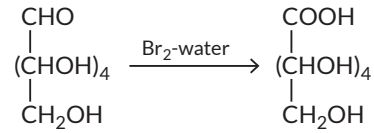
In starch, there is α-*D*-glycosidic linkage. Both the components of starch-amylose and amylopectin are polymer of α-*D*-glucose. On the other hand, cellulose is a linear polymer of β-*D*-glucose in which C_1 of one glucose unit is connected to C_4 of the other through β-*D*-glycosidic linkage.

28. (i)



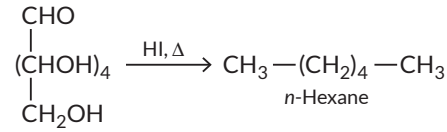
Glucose cyanohydrin

(ii) *D*-Glucose gets oxidised to carboxylic acid (gluconic acid) on reaction with bromine water.



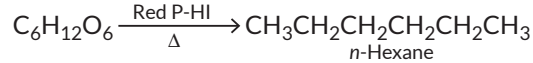
D-Glucose Gluconic acid

(iii) On prolonged heating with HI, *D*-glucose forms *n*-hexane.



D-Glucose *n*-Hexane

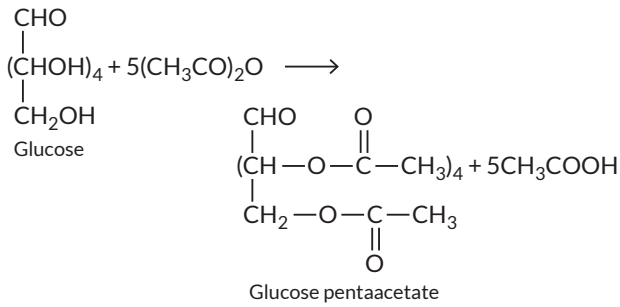
29. (i) Glucose when heated with red P and HI gives *n*-hexane.



n-Hexane

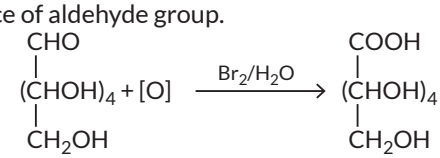
It indicates the presence of straight chain of six carbon atoms in glucose.

(ii) On acetylation with acetic anhydride, glucose gives a pentaacetate. This confirms that glucose contains five –OH groups.



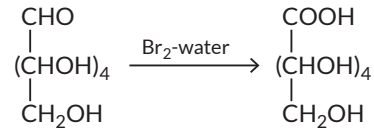
Glucose pentaacetate

(iii) Glucose on oxidation with a mild oxidising agent like bromine water gives gluconic acid containing the same six carbon atoms as present in glucose. This indicates presence of aldehyde group.



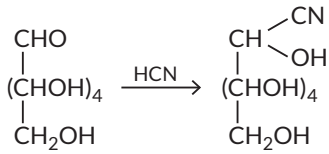
Gluconic acid

30. (a) *D*-Glucose gets oxidised to carboxylic acid (gluconic acid) on reaction with bromine water.



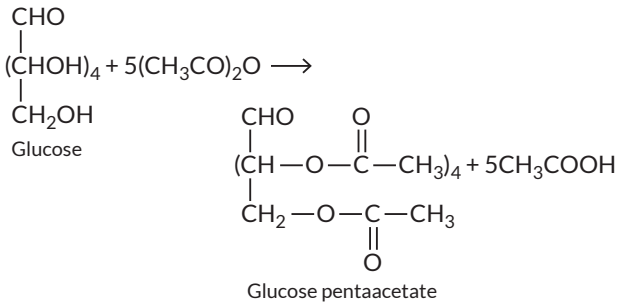
D-Glucose Gluconic acid

(b)

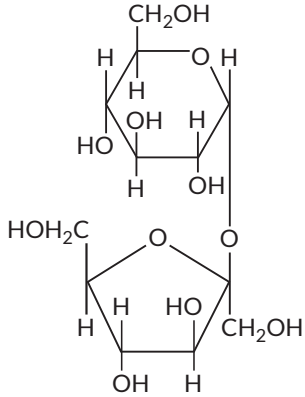


Glucose cyanohydrin

(c) On acetylation with acetic anhydride, glucose gives a pentaacetate. This confirms that glucose contains five –OH groups.



31. (i) The two monosaccharides are joined together by an oxide linkage formed by the loss of water molecule. Such linkage is called glycosidic linkage.



(ii) An equimolar mixture of glucose and fructose, obtained by hydrolysis of sucrose in presence of an acid or the enzyme invertase is called invert sugar.

(iii) These are the carbohydrates which on hydrolysis give 2-10 monosaccharides. For example, sucrose, lactose, maltose, etc.

32. (b): β-pleated sheet structure in proteins refers to secondary structure.

33. (c): α–Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into right-handed screw (helix) with $-NH_2$ group of each amino acid residue hydrogen bonded >C = O of adjacent turn of helix.

34. (d): Curdling of milk is an example of denatured protein and α-helix represents secondary structure of protein.

35. (b): Essential amino acids must be taken through diet as these cannot be synthesised in the body.

36. (b): Helix structure of proteins is stabilised by hydrogen bonds.

37. (c): Peptide linkage is present in proteins.

Key Points

➲ $\left[\begin{array}{c}O\\ \|\\ -C-NH-\end{array}\right]$ is called peptide linkage.

38. (c): Amino acid contains both basic ($-NH_2$) and acidic group (–COOH) hence, there are amphoteric in nature.

39. (c): Albumin is a globular protein. The chains of polypeptides coil around to give a spherical shape.

40. (b): α-Helix is a secondary structure of protein.

41. Peptide linkage is an amide linkage formed between —COOH group of one α-amino acid and $—NH_2$ group of the other amino acid by loss of a molecule of water whereas a linkage between two monosaccharides units through oxygen atom is called glycosidic linkage.

42. (a) The pair of stereoisomers which differ only in the configuration of the hydroxyl group at C_1 are called anomers.

(b) **Essential amino acids :** Amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine, leucine, etc.

(c) **Denaturation :** The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation.

During denaturation, secondary and tertiary structure of protein is destroyed but primary structure remains intact.

43. Characteristic differences between globular and fibrous proteins can be given as :

S.No.	Globular proteins	Fibrous proteins
1.	These are cross-linked proteins and are condensation product of acidic and basic amino acids.	These are linear condensation polymer.
2.	These are soluble in water, mineral acids and bases.	These are insoluble in water but soluble in strong acids and bases.
3.	These proteins have three dimensional folded structure. These are stabilised by internal hydrogen bonding, *e.g.*, egg albumin, enzymes.	These are linear polymers held together by intermolecular hydrogen bonds, *e.g.*, hair, silk.

44. Globular protein – Insulin
Fibrous protein – Keratin

45. As amino acids have both acidic (carboxyl group) and basic groups (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.

Answer Tips

➲ Amphoteric compounds react both with acids and bases.

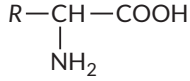
46. Acidic amino acids are those which contain more number of carboxyl groups as compared to amino groups whereas basic amino acids are those which contains more number of amino groups than carboxyl groups.

47. Peptide linkage

48. Essential amino acids : Amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine, leucine, etc.

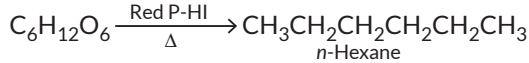
49. **Denaturation :** The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation.
During denaturation, secondary and tertiary structure of protein is destroyed but primary structure remains intact.

50. Organic compounds containing both amino ($-NH_2$) and carboxyl ($-COOH$) functional groups are called amino acids.



51. Disruption of native conformation of protein by changing its environment resulting in loss of biological activity is known as denaturation of protein.
Proteins are very sensitive to the action of heat, change of pH, presence of electrolytes and radiation (particularly short wavelengths).
Whenever proteins are subjected to such changes in the surroundings, they undergo some structural changes leading to the disruption of three dimensional structure. Thus, causes permanent loss of activity of proteins.
During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact.

52. (a) Glucose when heated with red P and HI gives *n*-hexane.



The above chemical reaction indicates the presence of straight chain of six carbon atoms in glucose.
(b) Peptide linkage

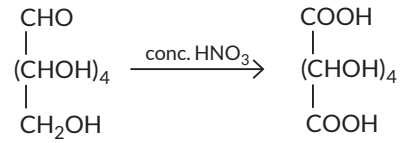
53. (i) The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation.
During denaturation, secondary and tertiary structure of protein is destroyed but primary structure remains intact. The normal shape of protein gets deformed because some of hydrogen bonds are broken and is referred as denatured proteins. *e.g.*, curdling of milk, coagulation of egg white on boiling etc.
(ii) **Essential amino acids :** Amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine, leucine, etc.

54. (a) As amino acids have both acidic (carboxyl group) and basic groups (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.
(b) In α-helix structure, intramolecular H-bonding takes place whereas in β-pleated structure, intermolecular H-bonding takes place.

Alternative Method

➲ α-Helix is having coiled structure while β-pleated is not planar but slightly pleated, *e.g.*, fibroin.

55. (a) On oxidation with nitric acid, *D*-glucose yields saccharic acid.



D-glucose *D*-saccharic acid

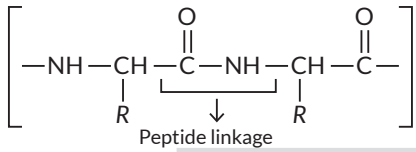
(b) As amino acids have both acidic (carboxy group) and basic groups (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.
(c) In α-helix structure, intramolecular H-bonding takes place whereas in β-pleated structure, intermolecular H-bonding takes place.

56. Proteins are the biomolecules of the living system made up of nitrogenous organic compounds by condensation polymerisation of α-amino acids.
On the basis of molecular structure, proteins are classified as :
(a) Fibrous proteins : In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, *e.g.*, keratin and myosin.
(b) Globular proteins : Globular proteins result when the polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, *e.g.*, insulin and albumins.

57. (i) Amylose is a linear condensation polymer of α-*D*-glucose in which C_1 of one glucose unit is attached to C_4 of the other through α-glycosidic linkage while amylopectin is a highly branched polymer in which α-*D*-glucose is linked with C_1-C_4 linkage and C_1-C_6 linkage is present between two linear chains.
(ii) Peptide linkage is an amide linkage formed between $-COOH$ group of one α-amino acid and $-NH_2$ group of the other amino acid by loss of a molecule of water whereas a linkage between two monosaccharides units through oxygen atom is called glycosidic linkage.
(iii) Characteristic differences between globular and fibrous proteins can be given as :

S.No.	Globular proteins	Fibrous proteins
1.	These are cross-linked proteins and are condensation product of acidic and basic amino acids.	These are linear condensation polymer.
2.	These are soluble in water, mineral acids and bases.	These are insoluble in water but soluble in strong acids and bases.
3.	These proteins have three dimensional folded structure. These are stabilised by internal hydrogen bonding, *e.g.*, egg albumin, enzymes.	These are linear polymers held together by intermolecular hydrogen bonds, *e.g.*, hair, silk.

58. (i) Proteins are the polymers of α-amino acids linked by amide formation between carboxyl and amino group. This is called peptide linkage or peptide bond, *e.g.*,



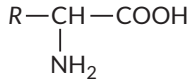
(ii) **Primary structure :** The specific sequence in which the various amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein.

(iii) **Denaturation :** The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation.

During denaturation, secondary and tertiary structure of protein is destroyed but primary structure remains intact.

59. Amino acids which cannot be synthesised in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine and leucine. There are ten essential amino acids. Amino acids which can be synthesised in the body are known as non-essential amino acids, *e.g.*, alanine and glutamic acids.

60. (i) Organic compounds containing both amino ($-NH_2$) and carboxyl (—COOH) functional groups are called amino acids.

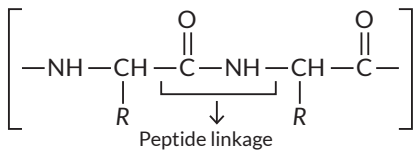


(ii) As amino acids have both acidic (carboxyl group) and basic groups (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.

(iii) Acidic amino acids are those which contain more number of carboxyl groups as compared to amino groups whereas basic amino acids are those which contains more number of amino groups than carboxyl groups.

(iv) Amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine, leucine, etc.

(v) Proteins are the polymers of α-amino acids linked by amide formation between carboxyl and amino group. This is called peptide linkage or peptide bond, *e.g.*,



61. Most of the chemical reactions which occur in living systems process at very slow rates under mild condition of temperature and pH. These reactions are catalysed by a group of biomolecules called enzymes.

62. Vitamin C is soluble in water and regularly excreted in urine and hence cannot be stored in body.

63. Vitamin D **64.** Vitamin C

65. Vitamin A **66.** Vitamin D

67. Vitamin C

68. Organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism are called vitamins.

69. The deficiency of vitamin A leads to xerophthalmia and night blindness. The deficiency of vitamin C leads to scurvy.

70. Organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism are called vitamins.

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) Fat soluble vitamins, (*e.g.*, vitamin A and D)

(ii) Water soluble vitamins, (*e.g.*, vitamin B and C)

71. (a) Maltose $\xrightarrow{\text{Hydrolysis}}$ Glucose + Glucose

(b) α-helix structure of protein stabilised by hydrogen bonding

(c) Vitamin B_{12}

72. Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) Fat soluble vitamins, (*e.g.*, vitamin A and D)

(ii) Water soluble vitamins, (*e.g.*, vitamin B and C)

Vitamin K is responsible for the coagulation of blood.

73. (b): Nucleoside contains pentose sugar and base whereas nucleotide contains pentose sugar, base as well as phosphate group.

Nucleoside = Base + Sugar

Nucleotide = Base + Sugar + Phosphate.

74. (d): Thymine is present in DNA but not in RNA.

75. (c): Nucleic acids are polymer of nucleotides.

76. (c): Nucleosides are composed of a pentose sugar and a nitrogenous base.

Key Points

- Nucleotide = Nucleoside + Phosphoric acid

77. A unit formed by attachment of base to 1′ position of sugar is known as nucleoside.

78. Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds as bases.

79. Nucleoside contains pentose sugar, and base whereas nucleotide contains pentose sugar, base as well as phosphate group.

Nucleoside = Base + Sugar

Nucleotide = Base + Sugar + Phosphate

Answer Tips

- Nucleoside + Phosphate = Nucleotide

80. Phosphodiester linkage **81.** Uracil

82. A nucleoside is consist of a purine or a pyrimidine base and a ribose or deoxyribose sugar connected via a β-glycosidic linkage.

83. Structural differences between DNA and RNA :

(i) The sugar in DNA is deoxyribose while that in RNA is ribose.

(ii) DNA has a double-stranded helical structure, while RNA has a single-stranded helical structure.

Functional differences between DNA and RNA :

(i) DNA is the chemical basis of heredity and is responsible for maintaining the identity of different species.

(ii) RNA molecules are responsible for protein synthesis but the message for the synthesis of a particular protein is present in DNA.

Answer Tips

- RNA is having one extra —OH in its sugar unit. Also bases present in RNA are adenine, cytosine, uracil and guanine, while in DNA these are thyamine, cytosine, adenine and guanine.

84. (a) As glucose forms a six-membered ring in which —CHO group combines with —OH group at C-5, penta-acetate of glucose does not react with hydroxylamine due to the absence of free —CHO group.
(b) Amino acids behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino groups) group in the same molecule.
(c) Water soluble vitamins must be taken regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.
(d) The two strands in DNA are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

85. (i) Characteristic differences between globular and fibrous proteins can be given as :

S.No.	Globular proteins	Fibrous proteins
1.	These are cross-linked proteins and are condensation product of acidic and basic amino acids.	These are linear condensation polymer.
2.	These are soluble in water, mineral acids and bases.	These are insoluble in water but soluble in strong acids and bases.
3.	These proteins have three dimensional folded structure. These are stabilised by internal hydrogen bonding, *e.g.*, egg albumin, enzymes.	These are linear polymers held together by intermolecular hydrogen bonds, *e.g.*, hair, silk.

(ii) Amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine, leucine, etc. The amino acids, which can be synthesised in the body, are known as non-essential amino acids.
(iii) The sugar in DNA is deoxyribose while that in RNA is ribose. DNA has a double-stranded helical structure, while RNA has a single-stranded helical structure.

86. (a) An equimolar mixture of glucose and fructose, obtained by hydrolysis of sucrose in presence of an acid or the enzyme invertase is called invert sugar.
(b) Native proteins : Protein purified from natural source which includes blood, plasma from animal etc.
(c) When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, we get a nucleotide.

87. (a) Actually, glucose exists in the cyclic hemiacetal form with only a small amount (< 0.05%) of the open chain form. Since, the concentration of the open chain form is low and its reaction with 2,4-DNP is reversible, therefore, formation of 2,4-DNP derivative cannot disturb the equilibrium to regenerate more of the open chain form from the cyclic hemiacetal form and hence, does not give this test.

Answer Tips

- 99.95% glucose exists in cyclic hemiacetal form.

(b) The two strands in DNA molecule are held together by the hydrogen bonds between purine base of one strand and pyrimidine base of the other and *vice versa*. Because of different sizes and geometries of the bases, the only possible pairing in DNA are G (guanine) and C (cytosine) through three H-bonds, *i.e.*, (C≡G) and between A (adenine) and T (thymine) through two H-bonds (*i.e.*, A = T). Due to this base-pairing principle, the sequence of bases in one strand automatically fixes the sequence of bases in the other strand. Thus, the two strands are complementary and not identical.
(c) The basic structural difference between starch and cellulose is of linkage between the glucose units. In starch, there is α-*D*-glycosidic linkage. Both the components of starch-amylose and amylopectin are polymers of α-*D*-glucose. On the other hand, cellulose is a linear polymer of β-*D*-glucose in which C1 of one glucose unit is connected to C4 of the other through β-*D*-glycosidic linkage.

88. (i)

S.No.	Amylose	Amylopectin
1.	15-20% part of starch	80-85% part of starch
2.	Made up of linear chain polymers of α-*D* glucose with C1-C4 linkage.	Made up of branched polymers of α-*D* glucose with C1-C4 and C1-C6 linkage between two chains
3.	Water soluble	Water insoluble

(ii) Characteristic differences between globular and fibrous proteins can be given as :

S.No.	Globular proteins	Fibrous proteins
1.	These are cross-linked proteins and are condensation product of acidic and basic amino acids.	These are linear condensation polymer.
2.	These are soluble in water, mineral acids and bases.	These are insoluble in water but soluble in strong acids and bases.
3.	These proteins have three dimensional folded structure. These are stabilised by internal hydrogen bonding, *e.g.*, egg albumin, enzymes.	These are linear polymers held together by intermolecular hydrogen bonds, *e.g.*, hair, silk.

(iii) Nucleoside contains pentose sugar, and base whereas nucleotide contains pentose sugar, base as well as phosphate group.
Nucleoside = Base + Sugar
Nucleotide = Base + Sugar + Phosphate

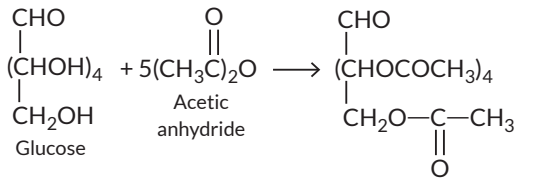
CBSE Sample Questions

1. **(d):** Open chain structure of glucose cannot explain existence of alpha and beta forms of glucose. **(0.77)**

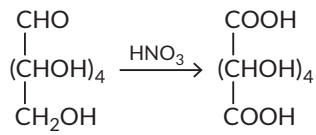
2. **(c):** Glycogen is a polymer of glucose. Hence, it is a polysaccharide. Glucose and maltose are monosaccharide whereas lactose is a disaccharide. **(0.77)**

3. **(c):** It undergoes inversion in the configuration on hydrolysis. Initially sucrose is *dextro*-rotatory but the mixture obtained after hydrolysis is *laevo*-rotatory. **(0.77)**

4. **(d):**



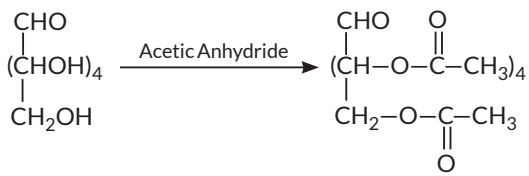
$+ 5CH_3COOH$



(0.77)

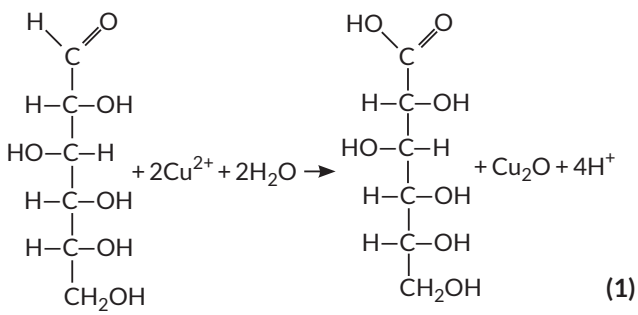
5. **(a):** Lactose and maltose are reducing sugars. **(1)**

6. (a) Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups. Since, it exists as a stable compound, five —OH groups should be attached to different carbon atoms



(1)

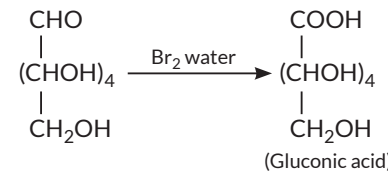
(b) Glucose reduces Fehling's reagent.



(1)

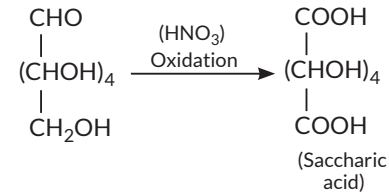
OR

(a)



(1)

(b)



(1)

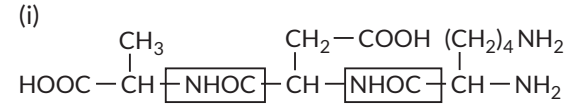
7. **(b)** **(1)**

8. **(d):** pH does not affect the primary structure of protein. pH changes affect the weak inter and intra molecular secondary linkage and hydrogen bonding. **(0.77)**

9. **(d)** **(1)**

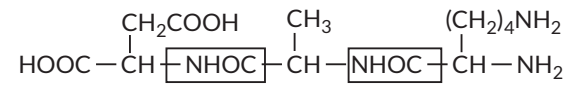
10. (i)

(a)



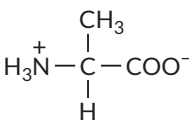
Peptide bond **(1)**

(b)



Peptide bond **(1)**

(ii)



(1)

11. **(b):** Amino acids form proteins and exist as zwitter ion. Thymine is a nitrogenous base in DNA, Insulin is a protein, a phosphodiester linkage is found in nucleic acids so also in DNA and uracil is nitrogenous base found in RNA which is a nucleic acid. **(0.77)**

12. **(a)** **(1)**

13. (a) Adenine bonds with thymine while cytosine bonds with guanine.
100 Adenine make bond with 100 Thymine
150 Cytosine make bond with 150 Guanine.
Total nucleotides = 100 + 100 + 150 + 150 = 500 **(1)**
(b) They studied the nucleotide composition of DNA. It was the same, so they concluded that the samples belong to same species. **(1)**
(c) A = T = 20% **(1)**
But G is not equal to C. So, virus is not a double helix.
The bases pairs are ATGC and not AUGC so it is not a RNA.
The virus is a single helix DNA virus. **(1)**

OR

According to Chargaff rule, all double helix DNA will have the same amount of A and T as well as C will be same amount as G. If the ratio of A or G and C is not maintained then, helix is single stranded.

Self Assessment

Case Based Questions (5 marks)

1. **Read the passage given below and answer the following questions :**

When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

The denaturation causes change in secondary and tertiary structures but primary structures remains intact. Examples of denaturation of protein are coagulation of egg white on boiling, curdling of milk, formation of cheese when an acid is added to milk.

(i) Mark the wrong statement about denaturation of proteins.

(a) The primary structure of the protein does not change.

(b) Globular proteins are converted into fibrous proteins.

(c) Fibrous proteins are converted into globular proteins.

(d) The biological activity of the protein is destroyed.

(ii) Which structure(s) of proteins remains(s) intact during denaturation process?

(a) Both secondary and tertiary structures

(b) Primary structure only

(c) Secondary structure only

(d) Tertiary structure only

(iii) α-Helix and β-pleated structures of proteins are classified as

(a) primary structure

(b) secondary structure

(c) tertiary structure

(d) quaternary structure.

(iv) Cheese is a

(a) globular protein (b) conjugated protein

(c) denatured protein (d) derived protein.

(v) Secondary structure of protein refers to

(a) mainly denatured proteins and structure of prosthetic groups

(b) three-dimensional structure, especially the bond between amino acid residues that are distant from each other in the polypeptide chain

(c) linear sequence of amino acid residues in the polypeptide chain

(d) regular folding patterns of continuous portions of the polypeptide chain.

A & R Questions (1 mark)

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

2. **Assertion :** DNA undergoes replication.
Reason : DNA contains cytosine and thymine as pyrimidine bases.

3. **Assertion :** α-Amino acids exist as dipolar ions or zwitter ions.
Reason : α-Amino acids are the building blocks of proteins.

Multiple Choice Questions (1 mark)

4. Which of the following B group vitamins can be stored in our body?

(a) Vitamin B_1 (b) Vitamin B_2

(c) Vitamin B_6 (d) Vitamin B_{12}

5. Which of the following statements is not true about glucose?

(a) It is an aldohexose.

(b) On heating with HI it forms *n*-hexane.

(c) It is present in furanose form.

(d) It does not give 2,4-DNP test.

6. Which of the following acids is vitamin C?

(a) Aspartic acid (b) Ascorbic acid

(c) Adipic acid (d) Saccharic acid

7. Which of the following reactions of glucose can be explained only by its cyclic structure?

(a) Glucose forms pentaacetate.

(b) Glucose reacts with hydroxylamine to form an oxime.

(c) Pentaacetate of glucose does not react with hydroxylamine.

(d) Glucose is oxidised by nitric acid to gluconic acid.

OR

In a protein molecule various amino acids are linked together by

(a) peptide bond (b) dative bond

(c) α-glycosidic bond (d) β-glycosidic bond.

VSA Type Questions (1 mark)

8. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain.
9. How do you explain the presence of all the six carbon atoms in glucose in a straight chain?
10. Why vitamin C must be supplied regularly in diet?
11. Sucrose is *dextro*-rotatory but the mixture obtained after hydrolysis is *laevo*-rotatory. Explain.

SA I Type Questions (2 marks)

12. Which force stabilises tertiary structure of protein?
13. What the terms *t*, *r* and m stand for in the name of RNA?
14. What are the objections against open chain structure of glucose?
15. Amino acids exist as zwitter ion but *o*- and *p*-aminobenzoic acids do not. Why?
16. How will you show that glucose contains a carbonyl group?

OR

What is the role of DNA in protein synthesis?

SA II Type Questions (3 marks)

17. (a) If one strand of a DNA has the sequences – ATGCTTCA – what is the sequence of the bases in the complementary strand?
    (b) What will be the sequence of bases on *m*RNA molecule synthesized on the following strand of DNA? TATCTACCTGGA
    (c) What anticodon sequences of *t*-RNAs are coded by the *m*-RNA with the following base sequence. CUU – AUG – GCU – UGG – CCC – UAA
18. How are proteins classified on the basis of molecular shape? Explain giving examples.
19. Draw structure of a nucleotide.
20. Define and classify vitamins. Name the diseases caused due to lack of any three of them.

OR

Name the chemical components which constitute nucleotide. Write any two functions of nucleotides in a cell.

Case Based Questions (4 marks)

21. **Read the passage given below and answer the following questions :**

The sequence of bases along the DNA and RNA chain establishes its primary structure which controls the specific properties of the nucleic acid. RNA molecule is usually a single chain of ribose-containing nucleotide. On the basis of X-ray analysis of DNA, J.D., Watson and F.H.C. Crick (shared noble prize in 1962) proposed a three dimensional secondary structure for DNA. DNA molecule is a long and highly complex, spirally twisted, double helix, ladder like structure. The two polynucleotide chains or strands are linked up by hydrogen bonding between the nitrogeneous base molecules of their nucleotide monomers. Adenine (purine) always links with thymine (pyrimidine) with the help of two hydrogen bonds and guanine (purine) with cytosine (pyrimidine) with the help of three hydrogen bonds. Hence, the two strands extend in opposite directions, *i.e.*, are antiparallel and complimentary.

(i) Name the base that is found in nucleotide of RNA only.
(ii) Write the main structural differences between DNA and RNA.
(iii) Name the bases present in RNA. Which one of these is not present in DNA?

OR

Write the main functional differences between DNA and RNA. Of the four bases, name those which are common to both DNA and RNA.

LA Type Questions (5 marks)

22. (i) Draw the structure of following :
    (a) sucrose (b) maltose
    (c) lactose
    (ii) Name the deficiency disease caused by
    (a) Vitamin A (b) Vitamin B_{12}
23. (a) Why is *D*-fructose used only for sweetening cold drinks and not hot ones?
    (b) How will you distinguish 1° and 2° hydroxyl groups present in glucose? Explain with reactions.
24. (i) How is glucose prepared?
    (ii) Fructose contains a keto group but still reduces Tollens' reagent. Why?
    (iii) What is essentially the difference between α-form and β-form of glucose? Explain giving structure.
25. How does DNA replicate? Describe the mechanism of replication. How is the process responsible for preservation of heredity?

OR

(a) Write the chemical equation for the reactions of glucose with :
(i) acetic anhydride and
(ii) ammoniacal silver nitrate solution.
(b) What do you understand by replication of DNA? How does DNA differ from RNA in terms of sugar moiety?

Detailed SOLUTIONS

1. **(i) (c)**

(ii) (b)

(iii) (b)

(iv) (c) : Cheese is a denatured protein.

(v) (b)

2. **(b):** DNA contains purines (A, G) and pyrimidines (T, C). The genetic information of the cell is contained in the sequence of base A, T, G and C in DNA molecule when a cell divides, DNA molecules replicate and make exact copies of themselves so that each daughter cell will have DNA identical to that of the parent cell.

3. **(b)**

4. **(d):** Vitamin B_{12} can be stored in our body because it is insoluble in water.

5. **(c) :** It is present in pyranose structure.

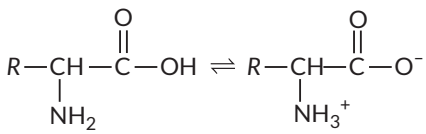
6. **(b):** Ascorbic acid is vitamin C.

7. **(c) :** The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free –CHO group. This property of glucose can be explained only by its cyclic structure.

OR

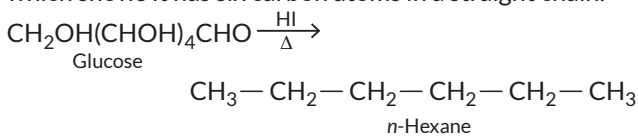
(a)

8. In aqueous solution carboxylic group loses a proton and amino group accepts proton to form zwitter ion.



(Zwitter ion)

9. On prolonged heating with HI, glucose gives *n*-hexane which shows it has six carbon atoms in a straight chain.



10. Vitamin C is water soluble hence it is readily excreted in urine and can't be stored in the body.

11. On hydrolysis, sucrose (*dextro*-rotatory) gives glucose (*dextro*-rotatory +52.5) and fructose (*laevo*-rotatory, –92.4°). Since, *laevo*-rotation is higher in magnitude, the mixture is *laevo*-rotatory.

12. H-bond, disulphide linkage, van der Waals' and electrostatic force stabilises tertiary (3°) structure of protein.

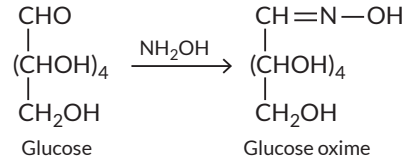
13. *t* for transfer, *r* for ribosomal and *m* for messenger.

14. (i) Despite having an aldehyde group, glucose doesn't give 2,4-DNP and Schiff's test and it doesn't form the hydrogen sulphite addition product with $NaHSO_3$.

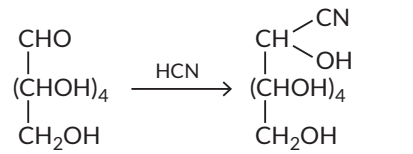
(ii) The pentaacetate doesn't react with hydroxylamine indicating absence of free —CHO group.

15. *o*- and *p*- aminobenzoic acids contain both weakly acidic (—COOH) and weakly basic ($—NH_2$) group due to the electron withdrawing nature of benzene ring. Hence, —COOH group cannot transfer H^+ ion to $—NH_2$ group. Hence, cannot form zwitter ion.

16. Glucose reacts with hydroxylamine to form an oxime and reacts with hydrogen cyanide to give cyanohydrin.



Glucose Glucose oxime



Glucose Glucose cyanohydrin

These reactions suggest that glucose contains a carbonyl group.

OR

Proteins are synthesised by RNA but the message for synthesis of a particular protein is present in DNA.

17. (a) We know that in DNA molecule, adenine (A) always pairs with thymine (T) and cytosine (C) always pairs with guanine (G). Thus, sequence of bases in one strand : A T G C T T C A

∴ Sequence of bases in the complementary strand : T A C G A A G T.

Thus, the sequence of bases in the complementary strand is TACGAAGT.

(b) We know that both in DNA and RNA, cytosine (C) pairs with guanine (G), Further, since RNA molecule does not contain thymine (T) but instead contains uracil (U), therefore, thymine (T) in DNA pairs with adenine (A) but adenine (A) in DNA must pair with uracil (U) in RNA. Thus, sequence of bases in DNA strand : TATCTACCTGGA

∴ Sequence of bases in *m*-RNA : AUAGAUGGACCU

Thus, the sequence of bases on the *m*-RNA strand is AUAGAUGGACCU.

(c) Codon sequences in *m*-RNA :

CUU – AUG – GCU – UGG – CCC – UAA

Since, anticodon sequence of *t*-RNA are complementary to the codon sequences on *m*-RNA.

∴ Anticodon sequence of *t*-RNAs :

GAA – UAC – CGA – ACC – GGG – AUU

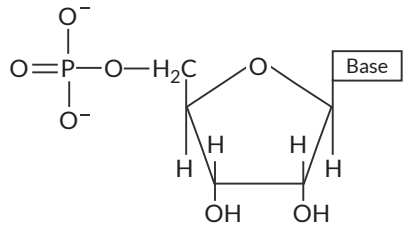
18. On the basis of molecular shape proteins are classified as follows :

(i) **Fibrous proteins :** When polypeptide chains run parallel and are held together by hydrogen and sulphide bonds then the fibre-like structure is formed. These are

insoluble in water. *e.g.*, keratin, myosin.

(ii) **Globular proteins :** In this, chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. *e.g.*, albumin, insulin.

19.



Nucleotide

20. Vitamins are defined as essential dietary substances required by an organism in minute quantities and their absence causes specific deficiency diseases. Vitamins cannot be synthesised by the body and have to be supplied in the food.

Vitamins are classified into two types :

(i) **Fat soluble vitamins :** These are oily substances not readily soluble in water. For example, vitamins A, D, E and K.

(ii) **Water soluble vitamins :** This group includes vitamins B (B-complex) and C. These are stored in the cells in much smaller amount.

Disease caused due to deficiency of vitamin can be tabulated as :

Name of vitamin	Deficiency disease
Vitamin A	Xerophthalmia
Vitamin B	Beri - Beri
Vitamin C	Scurvy

OR

A nucleotide is made up of nitrogen containing heterocyclic base, a pentose sugar and a phosphate group.

Important functions of nucleotides in a cell are :

(i) Nucleotides are building blocks of nucleic acids which are polynucleotides.

(ii) Some nucleotides act as energy carriers.

21. (i) Uracil

(ii) Structural differences between DNA and RNA :

(a) The sugar in DNA is deoxyribose while that in RNA is ribose.

(b) DNA has a double-stranded helical structure, while RNA has a single-stranded helical structure.

(iii) The bases present in RNA are adenine (A), guanine (G), cytosine (C) and Uracil (U). Uracil is not present in DNA.

OR

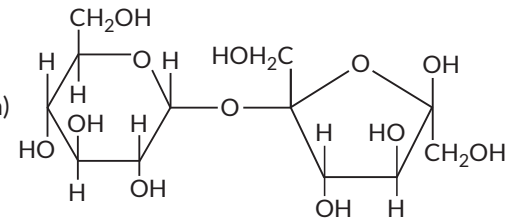
Functional differences between DNA and RNA :

(a) DNA is the chemical basis of heredity and is responsible for maintaining the identity of different species.

(b) RNA molecules are responsible for protein synthesis but the message for the synthesis of a particular protein is present in DNA. In DNA, thymine is present.

Common bases in DNA and RNA are adenine, guanine and cytosine.

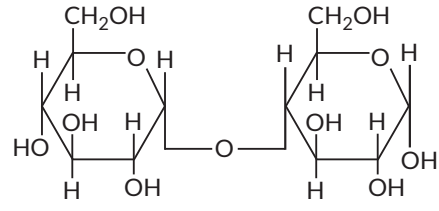
22. (i) (a)



α-*D*-Glucose β-*D*-Fructose

(Structure of sucrose)

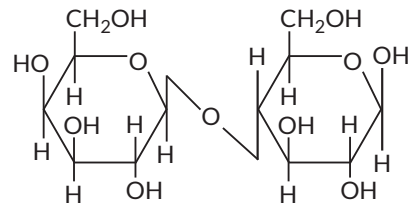
(b)



α-*D*-Glucose α-*D*-Glucose

(Structure of maltose)

(c)



β-*D*-Galactose β-*D*-Glucose

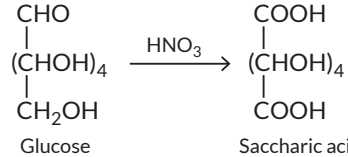
(Structure of lactose)

(ii) (a) Night blindness (b) Pernicious Anaemia

23. (a) Fructopyranose is the sweeter form of fructose. At higher temperatures the equilibrium shifts towards the less sweet furanose form.

$$\text{Pyranose} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Furanose}$$

(b) On oxidation with nitric acid, glucose yield a dicarboxylic acid, saccharic acid. This indicates presence of one primary (–OH) alcoholic group in glucose because only 1°(–OH) groups are oxidised to (–COOH) group with oxidation such as HNO_3 while 2°(–OH) groups need drastic conditions to oxidise. Thus, rest four (–OH) groups in glucose are 2°(–OH) groups.



Glucose Saccharic acid

24. (i) **From sucrose :**

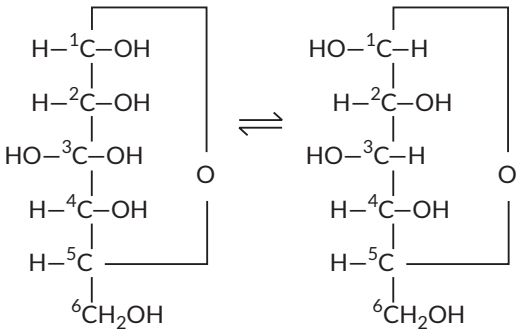
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

From starch :

$$\underset{\text{Sucrose}}{(C_6H_{10}O)_n} + nH_2O \xrightarrow[393\text{ K, 2-3 atm}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

(ii) In diluted alkaline solution fructose undergoes isomerisation to glucose *via* mannose. This is why fructose reduces Tollens' reagent and Fehling solution although it contains a keto group.

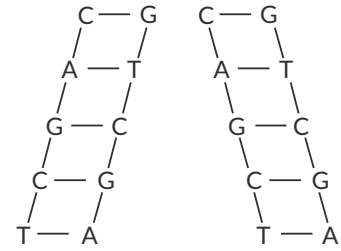
(iii) In α-*D* Glucose, the –OH group at C_1 is towards right whereas in β-glucose, the –OH group at C_1 is towards left. Such a pair of stereoisomers which differ in the configuration only at C_1 are called anomers.



α-*D*-(+) – Glucose β-*D*-(+) – Glucose

25. Replication is the process by which a single DNA molecule produces two identical copies of itself, during cell division. During this process, the two strands of the double helix first separate and each separated strand then serves as a template for the synthesis of new strand. Due to specificity of base - pair the sequence in the two new strands is complementary of each other.

In other words, replication leads to the production of two identical copies of DNA from a single parent DNA and a copy of each then passes on to the new cells resulting from cell division. In this way the hereditary effects are transmitted from one cell to another.



OR

(a) (i) $HOCH_2—(CHOH)_4—CHO + 5(CH_3CO)_2O \longrightarrow CH_3OCOCH_2—[CH(OCOCH_3)]_4—CHO$

Glucose; Acetic anhydride; Glucose pentaacetate

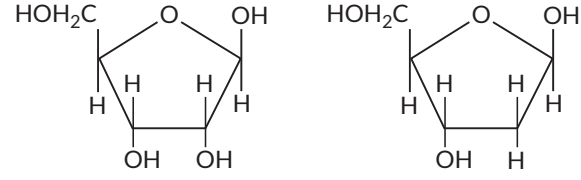
(ii) Glucose reduces ammoniacal silver nitrate solution (Tollens' reagent) to metallic silver.

$$HOCH_2—(CHOH)_4—CHO + [Ag(NH_3)_2]^+ + OH^- \longrightarrow HOCH_2—(CHOH)_4—COOH + 2Ag$$

Gluconic acid

(b) Replication is the process by which a single DNA molecule produces two identical copies of itself, during cell division.

In DNA molecules, the sugar moiety is β-*D*-2-deoxyribose whereas in RNA mole, it is β-*D*-ribose.



β-D-Ribose β-D-2-Deoxyribose

PRACTICE PAPER 1

General Instructions :

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple - choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case - based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. $\Lambda°$ ($ClCH_2COONa$) = 224 $ohm^{-1}\,cm^2\,mol^{-1}$, $\Lambda°$(NaCl) = 38.2 $ohm^{-1}\,cm^2\,mol^{-1}$, $\Lambda°$(HCl) = 203 $ohm^{-1}\,cm^2\,mol^{-1}$, what is the value of $\Lambda°(ClCH_2COOH)$?
   (a) 288.5 $ohm^{-1}\,cm^2\,mol^{-1}$
   (b) 289.5 $ohm^{-1}\,cm^2\,mol^{-1}$
   (c) 388.8 $ohm^{-1}\,cm^2\,mol^{-1}$
   (d) 59.5 $ohm^{-1}\,cm^2\,mol^{-1}$

2. Aldehydes, other than formaldehyde react with Grignard's reagent to give addition products which on hydrolysis give
   (a) tertiary alcohols
   (b) secondary alcohols
   (c) primary alcohols
   (d) carboxylic acids.

3. The term anomers of glucose refers to
   (a) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4)
   (b) a mixture of (*D*)-glucose and (*L*)-glucose
   (c) enantiomers of glucose
   (d) isomers of glucose that differ in configuration at carbon one (C-1).

4. Friedel–Crafts acylation of benzene with benzoyl chloride gives
   (a) $C_6H_5COCH_3$ (b) CH_3COCH_3
   (c) $C_6H_5COC_6H_5$ (d) none of these.

5. In the following sequence of reactions

$$CH_3CH_2CH_2Br \xrightarrow{KOH\ (alc.)} (A) \xrightarrow{HBr} (B) \xrightarrow{KOH(aq.)} (C)$$

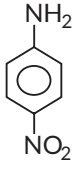
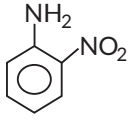
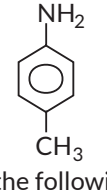
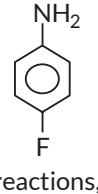
   The major product (*C*) is
   (a) propene (b) propyne
   (c) propan-1-ol (d) propan-2-ol.

6. Which of the following ions are coloured ?
   1. Cu^+ 2. Ti^{4+}
   3. Co^{2+} 4. Fe^{2+}
   (a) 1, 2, 3, 4 (b) 3, 4
   (c) 2, 3 (d) 1, 2

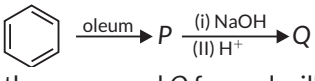
7. The rate of the reaction, $A + B + C \longrightarrow P$ is given by :

$$r = -\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/2}[C]^{1/4}.$$

   The order of the reaction is
   (a) 1 (b) 2 (c) 1/2 (d) 5/4

8. The most basic amine among the following is
   (a) 
   (b) 
   (c) 
   (d) 

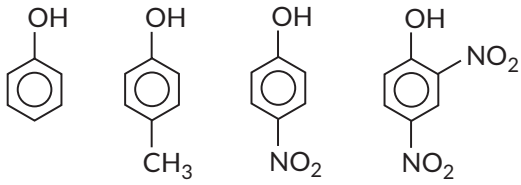
9. In the following sequence of reactions,



   the compound *Q* formed will be
   (a) aniline (b) phenol
   (c) benzaldehyde
   (d) benzene sulphonic acid.

10. The rate of a gaseous reaction is given by the expression $k[A]^2[B]^3$. The volume of the reaction vessel is reduced to one half of the initial volume. What will be the reaction rate as compared to the original rate *a*?
    (a) $\frac{1}{8}a$ (b) $\frac{1}{2}a$ (c) $2a$ (d) $32a$

11. The correct order of strength of acidity of the following compounds is



(i) (ii) (iii) (iv)

(a) (ii) > (i) > (iii) > (iv) (b) (i) > (ii) > (iii) > (iv)
(c) (iv) > (iii) > (ii) > (i) (d) (iv) > (iii) > (i) > (ii)

12. General electronic configuration of lanthanoids is
(a) $(n-2)f^{0-14}(n-1)s^2p^6d^{0-1}ns^2$
(b) $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$
(c) $(n-2)f^{0-14}(n-1)d^{10}ns^2$
(d) $(n-2)d^{0-1}(n-1)f^{0-14}ns^1$

13. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Reimer-Tiemann reaction is used to prepare salicylaldehyde from phenol.
Reason (R) : Reimer-Tiemann reaction involves nucleophilic substitution.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

14. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Carbonyl compounds have substantial dipole moments and are polar than ethers.
Reason (R) : The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral and a dipolar structures $>C=O \leftrightarrow >C^+—O^-$.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

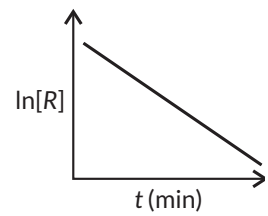
15. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : *D*-glucose is *dextro*-rotatory whereas *L*-glucose is *laevo*-rotatory.
Reason (R) : *D*-compounds are always *dextro* and *L*-compounds are always *laevo*-rotatory.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A): Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
Reason (R): For weak electrolyte, degree of dissociation increases with dilution of solution.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION-B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. For a certain chemical reaction, variation in the concentration, ln[*R*] *vs* time (min) plot is shown below :



For this reaction
(i) What is the order of reaction?
(ii) What are the units of rate constant, *k* for this reaction?
(iii) Give the relationship between *k* and $t_{1/2}$ of this reaction.
(iv) If initial concentration for this reaction becomes half, how will $t_{1/2}$ vary?

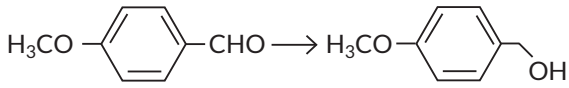
18. Calculate molarity and molality of a 13% solution (by weight) of sulphuric acid. Its density is 1.02 g cm^{-3}. (Atomic mass of H = 1, O = 16, S = 32)

19. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.

20. (i) When propanone is subjected to Wolff-Kishner reduction, what product will be obtained? Give chemical equation.
(ii) How will you convert acetaldehyde to acetone?

OR

(a) Suggest reagents to obtain the following product :



(b) In acylium ion, the structure $R-C\equiv O^+$ is more stable than $R-C^+=O$. Explain.

21. (a) Amino acids show amphoteric behaviour. Why?
(b) Write one difference between α-helix and β-pleated structures of proteins.

SECTION-C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. Explain why :
(i) $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic.
(ii) A solution of $[Ni(H_2O)_6]^{2+}$ is green but $[Ni(CN)_4]^{2-}$ is colourless.
(iii) The low spin tetrahedral complexes are rarely observed.

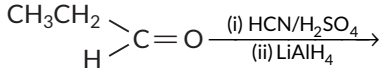
23. For the reaction,
$2AgCl_{(s)} + H_{2(g)}\ (1\ atm) \rightarrow 2Ag_{(s)} + 2H^+\ (0.1\ M) + 2Cl^-(0.1\ M)$
$\Delta G° = -43600$ J at 25 °C.
Calculate the e.m.f. of the cell.

24. (a) Phenol is acidic while hexanol is neutral towards a solution of NaOH. Why?
(b) *m*-Aminophenol is stronger acid than *o*-aminophenol. Explain.

OR

Name the different reagents needed to perform the following reactions :
(i) Phenol to benzene
(ii) Friedel-Crafts alkylation of anisole
(iii) Dehydrogenation of ethanol to ethanal

25. (a) Complete the following reaction with appropriate structure :



(b) Name the reagents used in the following reactions:
(i) $CH_3-CO-CH_3 \xrightarrow{?} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$
(ii) $C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$

26. (a) What is the basic structural difference between starch and cellulose?
(b) Sucrose $\xrightarrow{H^+}$ *A* + *B*
Identify products *A* and *B*.

27. Give reasons :
(a) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.
(b) Which will have higher boiling point 1-chloroethane or 2-methyl-2-chlorobutane?,
(c) Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?

28. (a) Rate constant, *k* for a first order reaction has been found to be 2.54×10^{-3} sec^{-1}. Calculate its $3/4^{th}$ life. (log 4 = 0.6020)
(b) How much time is required for the completion of a zero order reaction?
(c) How does the value of rate constant vary with reaction concentration for first order reaction?

SECTION-D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. For understanding the structure and bonding in transition metal complexes, the magnetic properties are very helpful. Low spin complexes are generally diamagnetic because of pairing of electrons, whereas high spin complexes are usually paramagnetic because of presence of unpaired electrons. Larger the number of unpaired electrons, stronger will be the paramagnetism. However magnetic behaviour of a complex can be confirmed from magnetic moment measurement. Magnetic moment $\mu = \sqrt{n(n+2)}$ B.M. where *n* = number of unpaired electrons. Greater the number of unpaired electrons, more will be the magnetic moment.
Answer the following questions :
(a) $[CoF_6]^{3-}$ is paramagnetic but $[Co(NH_3)_6]^{3+}$ is diamagnetic complex. Why?

OR

What are t_{2g} and e_g orbitals in octahedral complex and t_2 and *e* in tetrahedral complex?
(b) What is the geometry of the compound $[Pt(NH_3)_2Cl_2]$?
(c) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

30. The potential of each electrode is known as electrode potential. Standard electrode potential is the potential when concentration of each species taking part in electrode reaction is unity and the reaction is taking place at 298 K. By convention, the standard electrode potential of hydrogen (SHE) is 0.0 V. The electrode potential value for each electrode process is a measure of relative tendency of the active species in the process to remain in the oxidised/reduced form. The negative electrode potential means that the redox couple is stronger reducing agent than H^+/H_2 couple.

A positive electrode potential means that the redox couple is a weaker reducing agent than the H^+/H_2 couple. Metals which have higher positive value of standard reduction potential form the oxides of greater thermal stability.

Answer the following questions :

(a) What is standard electrode potential?

(b) Lithium metal is the strongest reducing agent. Why?

(c) Following two reactions can occur at cathode in the electrolysis of aqueous sodium chloride.

$Na^+ + e^- \rightarrow Na_{(s)}$, $E°_{red} = -2.71$ V

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$, $E°_{red} = -0.83$ V

Which reaction takes place preferentially and why?

OR

Given the standard electrode potentials,

$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V,

$Hg^{2+}/Hg = 0.79$ V

$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V

Arrange these metals in their increasing order of reducing power.

SECTION-E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt **any five** of the following:

(a) The enthalpies of atomisation of transition elements are high. Give reason.

(b) Draw the structure of chromate and dichromate ions.

(c) Give two reactions in which potassium dichromate acts as oxidising agent.

(d) Which transition metal of 3*d* series exhibits the largest number of oxidation states and why?

(e) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as transition element. Explain

(f) Orange solution of potassium dichromate turns yellow on adding sodium hydroxide to it. Give reason.

(g) Name the lanthanoids which show abnormally low value of third ionisation enthalpy.

32. (a) When is the value of van't Hoff factor more than one?

(b) An aqueous solution of glucose is made by dissolving 10 g of glucose ($C_6H_{12}O_6$) in 90 g of water at 303 K. If the vapour pressure of pure water at 303 K be 32.8 mm Hg, what would be the vapour pressure of the solution?

(c) How many gram of KCl should be required to be added to 1 kg of water to lower the freezing point to –8 °C? $K_f(H_2O) = 1.86$ K kg mol^{-1}, at. mass of K = 39, Cl = 35.5.

OR

(a) What weight of the non-volatile urea ($H_2N—CO—NH_2$) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

(b) 4% NaOH solution (mass/volume) and 6% urea solution (mass/volume) are equimolar but not isotonic. Why ?

33. Write one chemical reaction each to illustrate the following :

(i) Hofmann's bromamide reaction.

(ii) Gabriel phthalimide synthesis.

(iii) Before reacting aniline with HNO_3 for nitration, it is converted to acetanilide. Why is this done and how is nitroaniline obtained subsequently?

OR

(a) (i) Give one chemical test to distinguish between $CH_3 - CH_2 - NH_2$ and $CH_3 - NH - CH_3$.

(ii) Write the chemical reaction for the reduction of nitroethane by $LiAlH_4$.

(b) Write the chemical reaction equation stating the reaction conditions required for each of the following conversions.

(i) Methyl bromide to ethylamine

(ii) Aniline to phenol

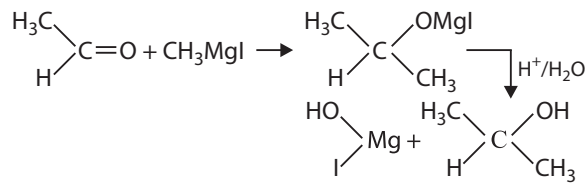
(iii) *p*-Toluidine to 2-bromo-4-methylaniline

Detailed SOLUTIONS

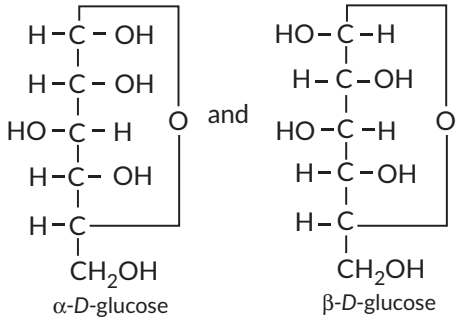
1. **(c) :** $\Lambda°(ClCH_2COOH) = \Lambda°(ClCH_2COONa) + \Lambda°(HCl) - \Lambda°(NaCl)$

$= 224 + 203 - 38.2 = 388.8$ ohm^{-1} cm^2 mol^{-1}

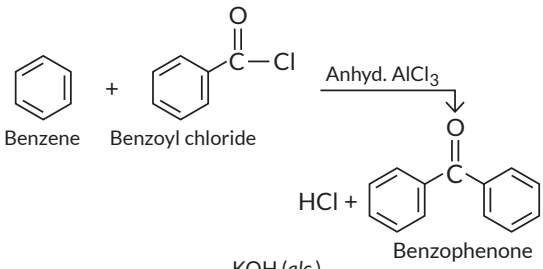
2. **(b):** Formaldehyde forms primary alcohol while all other aldehydes form secondary alcohols on reaction with Grignard's reagent followed by hydrolysis.



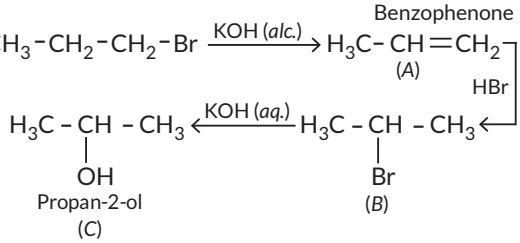
3. (d): Anomers are cyclic monosaccharides or glycosides that are epimers, differing from each other in the configuration at C-1, if they are aldoses or in the configuration at C-2 if they are ketoses.



4. (c):



5. (d):

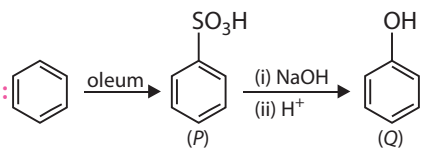


6. (b): Colour of transition elements is due to presence of unpaired electrons.

7. (d): Order of the reaction = $\frac{1}{2}+\frac{1}{2}+\frac{1}{4}=\frac{5}{4}$

8. (c): Among the given groups, only $-CH_3$ group is electron donating group hence it increases the electron density on nitrogen making it most basic.

9. (b):



10. (d): Rate = $k[A]^2[B]^3 = a$

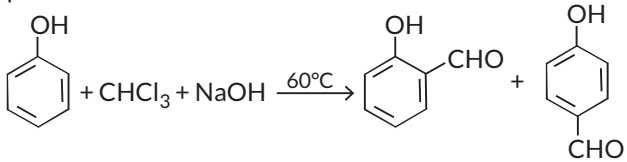
When volume is reduced to one half then conc. of reactants will be doubled.

Rate = $k[2A]^2[2B]^3 = 32\,k[A]^2[B]^3 = 32a$

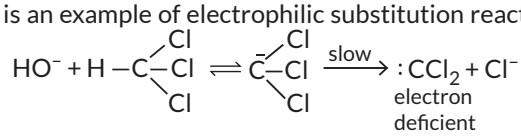
11. (d): Presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol and the presence of electron releasing groups such as alkyl group decreases the acidic strength of phenol.

12. (b)

13. (c): Reimer-Tiemann reaction – Formylation of phenols with chloroform in alkaline solution.



This is an example of electrophilic substitution reaction.



14. (a)

15. (c): *D*- and *L*- have no relation with the optical rotation. Carbohydrate having *D*-configuration may be either *dextro*-rotatory or *laevo*-rotatory *e.g.*, *D*-glucose is *dextro*-rotatory while *D*-fructose is *laevo*-rotatory.

16. (a): For weak electrolyte, Λ_m increases steeply on dilution due to increase in the number of ions (or the degree of dissociation).

17. (i) Reaction is of first order.

(ii) Units of rate constant, k is min^{-1}.

(iii) For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

(iv) No change in $t_{1/2}$ because half life period is independent of initial concentration for first order reaction.

18. Let mass of the solution = 100 g

Mass of the solute (w_2) = 13 g

and density of solution = 1.02 g cm^{-3}

$$\text{Volume of the solution} = \frac{\text{Mass of the solution}}{\text{Density of solution}}$$

$$= \frac{100\text{ g}}{1.02\text{ g cm}^{-3}} = \frac{100}{1.02}\text{ cm}^3$$

Molar mass of solute (H_2SO_4) = 1 × 2 + 32 + 16 × 4

= 98 g mol^{-1}

$$\text{Moles of the solute} = \frac{13}{98}\text{ mol}$$

$$\text{Molarity} = \frac{\text{Moles of the solute}}{\text{Volume of solution (in L)}}$$

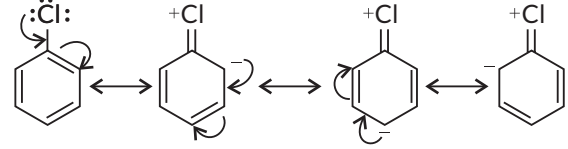
$$= \frac{13}{98}\times\frac{1000}{\frac{100}{1.02}} = \frac{13}{98}\times 1000\times\frac{1.02}{100} = 1.353\text{ M}$$

Now mass of solvent = 100 – 13 = 87 g

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

$$= \frac{13}{98}\times\frac{1000}{87} = 1.52\text{ m}$$

19. In haloarenes, –ve charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution. The electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



Haloalkanes have electrophilic carbon centre due to polarity of $C\overset{\delta+}{\rightarrow}\overset{\delta-}{X}$ bond.

20. (i) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[alc.\ KOH]{H_2N-NH_2} CH_3-CH_2-CH_3$
Propanone → Propane

(ii) $CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow[-CO_2,\ -H_2O]{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow[-CaCO_3]{\text{Dry distillation}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
Acetaldehyde → Acetone

OR

(a) $NaBH_4/CH_3OH$

(b) Both C and O are non-metals and try to complete their octet. In $R-C\equiv O^+$, each atom has complete octet whereas in $R-C^+=O$, carbon atom has incomplete octet.

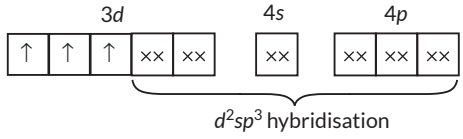
21. (a) As amino acids have both acidic (carboxy group) and basic groups (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.

(b) In α-helix structure, intramolecular H-bonding takes place whereas in β-pleated structure, intermolecular H-bonding takes place.

22. (i) The oxidation state of Cr in the complex is +3.

Cr^{3+} : [Ar] $3d^3$

$[Cr(NH_3)_6]^{3+}$:

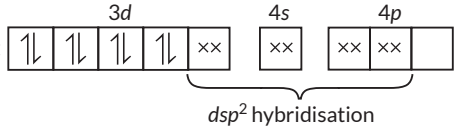


In this complex, three unpaired electrons are present, hence it is paramagnetic.

The oxidation state of Ni in the complex is +2.

Ni^{2+} : [Ar] $3d^8$

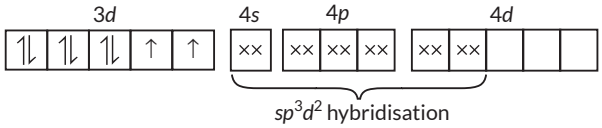
$[Ni(CN)_4]^{2-}$:



As CN^- is a strong field ligand, unpaired electrons are paired up, hence it is diamagnetic.

(ii) H_2O is a weak field ligand hence, $[Ni(H_2O)_6]^{2+}$ is an outer-orbital complex. The complex has two unpaired electrons. The *d-d* transition is possible. Hence, the compound is coloured.

$[Ni(H_2O)_6]^{2+}$:



In $[Ni(CN)_4]^{2-}$, CN^- is a strong field ligand. The unpaired electrons are paired up. No unpaired electrons are present, *i.e.*, *d-d* transition is not possible, hence the complex is colourless.

(iii) In tetrahedral coordination entity formation, the *d*-orbital splitting is smaller. Consequently, the orbital splitting energies are not sufficiently large to force pairing and therefore, low spin configurations are rarely observed.

23. $\Delta G^\circ = -nFE^\circ_{cell}$

$$E^\circ_{cell} = \frac{\Delta G^\circ}{-nF} = \frac{-43600}{-2\times 96500} = 0.226\ V$$

$2AgCl_{(s)} + H_{2(g)}(1\ atm) \longrightarrow 2Ag_{(s)} + 2H^+(0.1\ M) + 2Cl^-(0.1\ M)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Product]}{[Reactant]}$$

$$= 0.226 - \frac{0.0591}{2}\log\frac{(0.1)^2}{(1)}\times(0.1)^2$$

$$= 0.226 - \frac{0.0591}{2}\log(10^{-4})$$

$$= 0.226 - \frac{0.0591}{2}(-4) = 0.226 + 0.1182 = 0.3442\ V$$

Hence, e.m.f. of the cell is 0.3442 V.

24. (a) The phenoxide ion formed after loss of proton from phenol is resonance stabilised and thus, phenol loses H^+ ion to show acidic character.

$C_6H_5OH \longrightarrow \underset{\text{Resonance stabilised}}{C_6H_5O^-} + H^+$

On the other hand, alkoxide ion formed from hexanol shows no such resonance stabilisation and is unstable.

(b) In substituted phenols, the presence of electron releasing group decreases the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para*-positions. It is due to the increased negative charge in phenoxide ion. Thus, *m*-aminophenol is stronger acid than *o*-aminophenol.

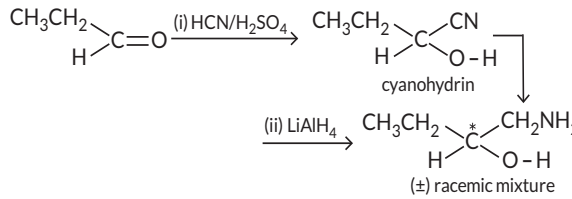
OR

(i) Zinc dust

(ii) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and $AlCl_3$ (anhy.)

(iii) Cu/573 K

25. (a)



(b) (i) Lithium aluminium hydride ($LiAlH_4$)

(ii) Alkaline potassium permanganate (alk. $KMnO_4$)

26. (a) Starch consists of two components, *i.e.*, amylose and amylopectin. Amylose is a linear polymer of α-*D*-(+) glucose in which C_1 of one glucose unit is connected to C_4 of the other glucose unit through α-glycosidic linkage. Amylopectin has similar structure but it has branched chain structure. Chain is formed by C_1-C_4 glycosidic linkage and branching occurs by C_1-C_6 glycosidic linkage.

Cellulose, on the other hand, is a straight chain polysaccharide composed of β-*D*-glucose and the

monomeric glucose units are linked together by $C_1 - C_4$ β-glycosidic linkage.

(b) Sucrose $\xrightarrow{H^+}$ $(CHOH)_4$(CHO, CH_2OH) + $C{=}O$(CH_2OH, $(CHOH)_3$, CH_2OH)

D-Glucose (*A*) + *D*-Fructose (*B*)

27. (a) Since, I^- ion is a better leaving group than Br^- ion therefore, CH_3CH_2I reacts faster than CH_3CH_2Br in S_N2 reaction with OH^- ion.

(b) The boiling points of haloalkanes increase with increase in molecular mass and length of chain.

Hence, boiling point of 2-methyl-2-chlorobutane is higher than 1-chloroethane.

(c) Benzyl chloride gets easily hydrolysed by *aq*. NaOH due to the formation of stable benzyl carbocation. But due to partial double bond character of C—Cl bond in chlorobenzene, it does not hydrolyse.

28. (a) The integrated rate equation for first order reaction is

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) \Rightarrow k = \frac{2.303}{t}\log\left(\frac{a}{a-\frac{3}{4}a}\right)$$

$$\Rightarrow \quad k = \frac{2.303}{t_{3/4}}\log\left(\frac{a}{0.25a}\right)$$

$$t_{3/4} = \frac{2.303}{2.54\times10^{-3}}\times\log\left(\frac{1}{0.25}\right) = 546\text{ s}$$

Therefore, the 3/4th life of the reaction is 546 seconds.

(b) Time required for the completion of a zero order reaction is $\frac{[A]_0}{k}$ units of time.

(c) Rate constant is independent of the concentration of the reactants for first order reaction.

29. (a) $[CoF_6]^{3-}$ is an outer orbital complex and it contains 4 unpaired electrons so, it is paramagnetic while $[Co(NH_3)_6]^{3+}$ is an inner orbital complex and it does not contain any unpaired electron so, it is a diamagnetic complex.

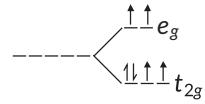
OR

Under the influence of ligands, when complex formation occurs, the five degenerate *d*-orbitals are split into two types of *d*-orbitals t_{2g} (three degenerate orbitals, d_{xy}, d_{yz} and d_{zx}) and e_g (two degenerate orbitals, d_{z^2} and $d_{x^2-y^2}$). Both sets have different energies.

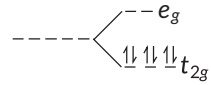
In octahedral complexes, t_{2g} orbitals possess low energy in comparison to e_g orbitals while in tetrahedral complexes, t_2 orbitals possess high energy in comparison to *e* orbitals.

(b) $[Pt(NH_3)_2Cl_2]$ has dsp^2 hybridisation leads to square planar geometry.

(c) $[Fe(H_2O)_6]^{2+}$ – H_2O is weak field ligand, Δ_o small, light green.



$[Fe(CN)_6]^{4-}$ – CN^- is strong field ligand, Δ_o large (absorbs near UV), pale yellow.



30. (a) The reduction potential of electrode when the concentration of the ions in solution is 1 mol L^{-1} and temperature is 298 K is called standard reduction potential ($E°_{red}$) or standard electrode potential ($E°$).

(b) Lithium metal is strongest reducing agent, because Li has lowest reduction potential *i.e.*, $E°_{Li^+/Li} = -3.05$ V.

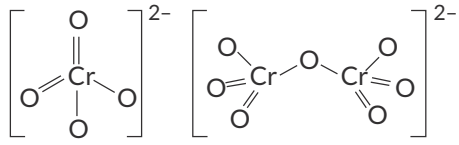
(c) $E°_{red}$ for water is higher than that of sodium so, reduction of water takes place in preference to reduction of sodium.

OR

Lower the electrode potential of a metal, greater is reducing power. The metals are arranged in the decreasing order of their electrode potentials.

Ag < Hg < Cr < Mg < K

31. (a) As transition metals have a large number of unpaired electrons in the *d*-orbitals of their atoms they have strong interatomic attractions or metallic bonds. Hence, they have high enthalpy of atomisation.

(b) 

Chromate ion Dichromate ion

(c) (i) $6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

(ii) $3Sn^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$

(d) Manganese has maximum number of unpaired electrons and it exhibits the largest number of oxidation states. Mn shows all the oxidation states from +2 to +7.

(e) Scandium ($Z = 21$) has incompletely filled 3*d*-orbitals in the ground state ($3d^1$). Hence, it is considered as a transition element.

(f) When the pH of the solution of potassium dichromate is decreased, the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $Cr_2O_7^{2-}$ ions.

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \rightleftharpoons \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O$$

(g) Third ionization enthalpy of lanthanoid is low if it leads to stable empty, half-filled or completely filled configuration, as indicated by the abnormally low third ionization enthalpies of La, Gd, and Lu.

32. (a) When the solute molecules undergo dissociation in the solution then, van't Hoff factor is more than 1.

(b) Here, $W_A = 90$ g, $W_B = 10$ g

$M_B = 72 + 12 + 96 = 180$

$P°$ = 32.8 mm Hg, M_A = 18

$$M_B = \frac{W_B M_A}{W_A} \times \frac{P^\circ}{P^\circ - P_S}$$

$$180 = \frac{10 \times 18}{90} \times \frac{32.8}{32.8 - P_S}$$

or $$32.8 - P_S = \frac{10 \times 18 \times 32.8}{90 \times 180} = 0.36$$

P_S = 32.8 – 0.36 = 32.44 mm Hg

(c) w_2 = ?, i = 2 (for KCl)

w_1 = 1 kg = 1000 g, K_f = 1.86 K kg mol^{-1}

M_2 (KCl) = 39 + 35.5 = 74.5 g mol^{-1}, ΔT_f = 8

$$\Delta T_f = \frac{w_2}{M_2} \times \frac{1000}{w_1} \times K_f \times i$$

$$w_2 = \frac{\Delta T_f \times M_2 \times w_1}{1000 \times K_f \times i} = \frac{8 \times 74.5 \times 1000}{1000 \times 1.86 \times 2} = \frac{298}{1.86}$$

= 160.21 g

OR

(a) Given :

$p°$ = 100, w_A = 100 g ; p_s = 75, w_B = ?

For urea, M_B = 60 g mol^{-1}

For water, M_A = 18 g mol^{-1}

$$\frac{p^\circ - p_s}{p_s} = \frac{n_B}{n_A} = \frac{w_B / M_B}{w_A / M_A} \quad \therefore \quad \frac{25}{75} = \frac{w_B / 60}{100 / 18}$$

or w_B = 111 g

Molality of the solution

$$= \frac{111\,\text{g}}{60\,\text{g mol}^{-1}} \times \frac{1}{100\,\text{g}} \times 1000\,\text{g kg}^{-1}$$

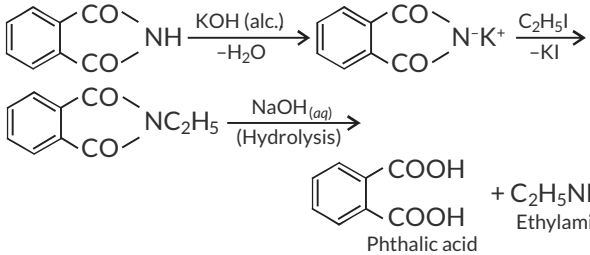
= 18.5 mol kg^{-1} or 18.5 m

(b) Both the solutions, 4% NaOH (*W/V*) and 6% urea (*W/V*) have same concentration (1 M) but these are not isotonic because NaOH undergoes dissociation in solution. Therefore, number of particles in NaOH solution is more than that in urea solution.

33. (i) $CH_3CONH_2 + Br_2 + 4KOH \longrightarrow$
Acetamide

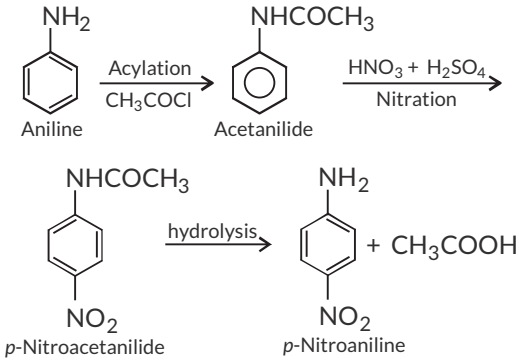
$$CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

(ii) **Gabriel phthalimide synthesis :** In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an N-alkylpthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.



This synthesis is very useful for the preparation of pure aliphatic primary amines. However, aromatic primary amines cannot be prepared by this method.

(iii) Aniline in strongly acidic medium is protonated to form anilinium ion which is ring deactivating and a *meta* directing group. So, besides the *o/p* derivatives significant amount of meta derivative is formed. So, in order to get *o/p* derivative aniline is first acetylated and converted to acetanilide. Nitro aniline is obtained by reacting acetanilide with HNO_3 and H_2SO_4 followed by hydrolysis.



OR

(a) (i) Each compound is warmed separately with few drops of chloroform and alcoholic KOH. $CH_3CH_2NH_2$ gives offensive smell of carbylamine.

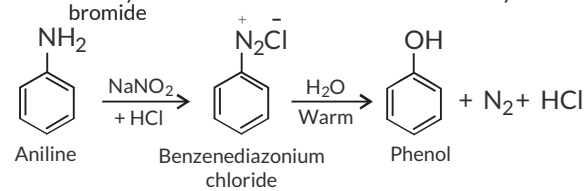
$$CH_2CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Warm}} CH_3CH_2NC + 3KCl + 3H_2O$$

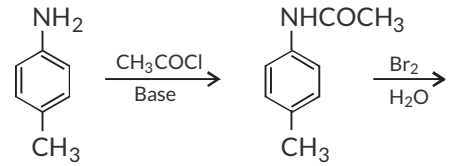
CH_3NHCH_3 being a secondary amine does not give carbylamine test.

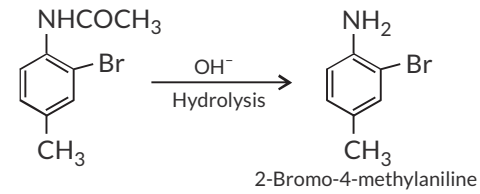
$$CH_3NHCH_3 \xrightarrow{CHCl_3 + KOH} \text{No reaction}$$

(ii) $C_2H_5NO_2 \xrightarrow[[6\,H]]{LiAlH_4} C_2H_5NH_2 + 2H_2O$
Nitroethane → Ethylamine

(b) (i) $CH_3Br \xrightarrow[\Delta]{\text{Alc. KCN}} CH_3CN \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2NH_2$
Methyl bromide → Ethylamine

(ii)


(iii)




PRACTICE PAPER 2

General Instructions :

Read the following instructions carefully.

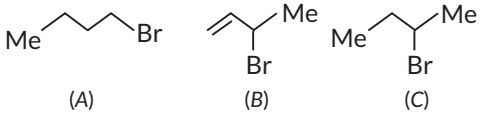
(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple - choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case - based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Consider the following bromides :



(A) (B) (C)

The correct order of S_N1 reactivity is
(a) $A > B > C$ (b) $B > C > A$
(c) $B > A > C$ (d) $C > B > A$

2. Which one of the following ions is coloured?
(a) Sc^{3+} (b) Ti^{4+}
(c) Zn^{2+} (d) V^{2+}

3. If the volume of the container is decreased to $\frac{1}{3}$rd of the original volume, by how much will the rate change for the elementary reaction?

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

(a) 9 times increase (b) 9 times decrease
(c) 27 times increase (d) 27 times decrease

4. A compound $C_6H_{14}O_2$ has two tertiary alcoholic groups. The IUPAC name of this compound is
(a) 2, 3-dimethyl - 1, 2-butanediol
(b) 3, 3-dimethyl - 1, 2-butanediol
(c) 2, 3-dimethyl - 2, 3-butanediol
(d) 2-methyl - 2, 3-pentanediol.

5. Which of the following options is incorrect?
(a) $[Ni(CO)_4]$: Tetrahedral, paramagnetic
(b) $[Ni(CN)_4]^{2-}$: Square planar, diamagnetic
(c) $[Ni(CO)_4]$: Tetrahedral, diamagnetic
(d) $[NiCl_4]^{2-}$: Tetrahedral, paramagnetic

6. Chlorination of toluene in presence of light and heat followed by treatment with aqueous NaOH gives
(a) *o*-cresol
(b) *p*-cresol
(c) 1, 3, 5-trihydroxytoluene
(d) benzoic acid.

7. $E°_{(Li^+/Li)} = -3.05$ V; $E°_{(Ba^{2+}/Ba)} = -2.73$ V; $E°_{(Mg^{2+}/Mg)} = -2.37$ V
The correct order as per reducing power is
(a) Li > Ba > Mg (b) $Li^+ > Ba^{2+} > Mg^{2+}$
(c) Mg > Ba > Li (d) $Mg^{2+} > Ba^{2+} > Li^+$

8. Glucose $\xrightarrow{HCN}$ $\xrightarrow{Hydrolysis}$ $\xrightarrow{HI/heat}$ A ; A is
(a) heptanoic acid (b) 2-iodohexane
(c) heptane (d) heptanol.

9. If acetyl chloride is reduced in the presence of $BaSO_4$ and Pd, then
(a) CH_3CHO is formed
(b) CH_3CH_2OH is formed
(c) CH_3COOH is formed
(d) CH_3COCH_3 is formed.

10. In the reaction, $H_2 + I_2 \longrightarrow 2HI$, what is the rate of appearance of HI, if rate of disappearance of H_2 is 10^{-6} mol L^{-1} s^{-1}?
(a) 10^{-6} mol L^{-1} s^{-1} (b) 2×10^{-6} mol L^{-1} s^{-1}
(c) 0.5×10^{-6} mol L^{-1} s^{-1} (d) 10^{-7} mol L^{-1} s^{-1}

11. In an octahedral crystal field, the t_{2g} orbitals are
(a) raised in energy by 0.4 Δ_o
(b) lowered in energy by 0.4 Δ_o
(c) raised in energy by 0.6 Δ_o
(d) lowered in energy by 0.6 Δ_o.

12. Propan-1-ol can be prepared from propene by
(a) H_2O/H_2SO_4
(b) $Hg(OAc)_2/H_2O$ followed by $NaBH_4$
(c) B_2H_6 followed by H_2O_2
(d) Br_2/H_2O

13. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Aliphatic primary amines can be prepared by Gabriel phthalimide synthesis.
Reason (R) : Aryl halides undergo nucleophilic substitution with the anion formed by phthalimide.

Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

14. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Most of the trivalent lanthanoids ions are coloured both in the solid state and in aqueous solution.
Reason (R) : The elements with *xf* electrons have a similar colour to those of (14 – *x*)*f* electrons.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

15. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Alanine is one of the basic units of protein.
Reason (R) : Alanine is an essential amino acid.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
Reason (R) : Aromatic aldehydes are almost as reactive as formaldehyde.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION-B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. What happens when
(i) aniline is treated with benzaldehyde
(ii) a mixture of alcohol and ammonia is passed over heated aluminium oxide as catalyst?

18. Rate constant of the first order reaction is $6.93 \times 10^{-3}\ s^{-1}$. Calculate
(i) half-life.
(ii) time of 75% completion of reaction.

OR

Differentiate between the rate of a chemical reaction and the rate constant for the reaction.

19. Give reasons for the following :
(i) The transition metals form interstitial compounds.
(ii) Silver halides find use in photography.

20. How many chiral compounds are possible on monochlorination of 2-methylbutane?

21. State the significance of primary and secondary structures of proteins.

SECTION-C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write the overall reaction.
[Given : $E^\circ_{Na^+/Na} = -2.71$ V, $E^\circ_{H_2O/H_2} = -0.83$ V, $E^\circ_{Cl_2/Cl^-} = +1.36$ V, $E^\circ_{H^+/H_2/H_2O} = +1.23$ V]

23. Explain that although —NH_2 group is *ortho* and *para* directing, but in presence of concentrated HCl aniline undergoes bromination giving *m*-bromoaniline.

24. (i) Differentiate between molarity and molality of solution.
(ii) Molarity of H_2SO_4 is 18 M. If its density is 1.8 g cm^{-3}, calculate its concentration in mol kg^{-1} in solvent (H_2O), *i.e.*, molality.

25. Give reasons for the following observations :
(i) Cerium (atomic number = 58) forms tetra-positive ion, Ce^{4+} in aqueous solution.
(ii) The second and third members in each group of transition elements have similar atomic radii.
(iii) Which of the following ions are expected to be coloured and why?
Cu^+, Fe^{2+}, Mn^{2+}, Cr^{3+}, Sc^{3+}, Ti^{4+}

26. (a) Why is *D*-fructose used only for sweetening cold drinks and not hot ones?
(b) How will you distinguish 1° and 2° hydroxyl groups present in glucose? Explain with reactions.
(c) How do you explain the presence of all the six carbon atoms in glucose in a straight chain?

27. (i) Write the product formed when *p*-nitro-chlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.
(ii) Why *dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation towards nucleophilic substitution reactions?
(iii) Why C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in H_3C—Cl?

OR

(a) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(b) Write a chemical test to distinguish between :
(i) Chlorobenzene and benzyl chloride
(ii) Chloroform and carbon tetrachloride

28. In a pseudo first order hydrolysis of ester in water, the following results are obtained :

t (in seconds)	0	30	60	90
[Ester] in M	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

SECTION-D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. Dialkyl ether reacts with an excess of hydrogen halide to give alkyl halides.

$R - O - R + HX \longrightarrow R - X + R - OH$

$R - OH + HX \longrightarrow R - X + H_2O$

This reaction is an example of nucleophillic substitution reaction.

Mixed ether containing primary or secondary alkyl group when heated with hydrogen halide, the lower alkyl group forms halide and the higher alkyl group forms alcohol.

Answer the following questions :

(a) Name the products formed when ethylphenyl ether is boiled with conc. HBr.

OR

Which products are formed on heating *tert*-butylmethyl ether with HI?

(b) How many moles of ethyl iodide are formed on heating diethyl ether with conc. HI?

(c) Name the organic compound with molecular formula, $C_4H_{10}O$ which does not react with Na while with excess of HI, it gives two types of alkyl halides. Also, write chemical reaction to explain this.

30. Elevation in boiling point describes the phenomenon that boiling point of a liquid (a solvent) will be higher when another compound is added to it, which means a solution has higher boiling point than a pure solvent. This happens whenever a non-volatile solute (such as salt) is added to pure solvent (such as water). For example, the addition of 3 g of a substance to 100 g CCl_4 (M = 154 g mol^{-1}) raises the boiling point of CCl_4 by 0.60°C. K_b (CCl_4) is 5.03 K kg mol^{-1}. Given : K_f (CCl_4) = 31.8 K kg mol^{-1} and ρ (solution) = 1.64 g cm^{-3}.

Answer the following questions :

(i) What is the molality of solution?

(ii) What is the freezing point depression of the solution?

(iii) What will be the molar mass (g mol^{-1}) of substance?

OR

At 298 K, what is the osmotic pressure of solution?

SECTION-E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt **any five** of the following:

(a) Anhydrous $CuSO_4$ is white while hydrated $CuSO_4$ is blue in colour.

(b) Arrange the following complexes in order of decreasing conductivity :

$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_6]Cl_3$,

$[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_5Cl]Cl_2$

(c) Write the name of linkage isomer of

$[Co(ONO)(NH_3)_5]^{2+}$.

(d) $[Ti(H_2O)_6]Cl_3$ is violet in colour but becomes colourless on heating.

(e) Geometrical isomerism is not possible for tetrahedral complexes. Explain.

(f) Write the IUPAC name and indicate the shape of complex ion $[Co(en)_2Cl(ONO)]^+$.

[At. no. of Co = 27]

(g) Name the compound used for the estimation of Ca^{2+} and Mg^{2+} ions present in hard water.

32. (a) When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.

(Specific conductance of 0.1 M KCl = 1.29×10^{-2} ohm^{-1} cm^{-1})

(b) Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ°_m for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

OR

(a) For the reaction,

$2AgCl_{(s)} + H_{2(g)}$ (1 atm) $\rightarrow 2Ag_{(s)} + 2H^+$ (0.1 M) + $2Cl^-$(0.1 M)

ΔG° = – 43600 J at 25 °C.

Calculate the e.m.f. of the cell.

(b) Write down the electrode process when aqueous solutions of the given halides are electrolysed :

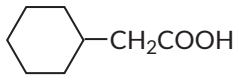
(i) $NaCl_{(aq)}$ (ii) $NaBr_{(aq)}$ (iii) $NaF_{(aq)}$

33. Two moles of organic compound '*A*' on treatment with a strong base gives two compounds '*B*' and '*C*'. Compound '*B*' on dehydrogenation with Cu gives

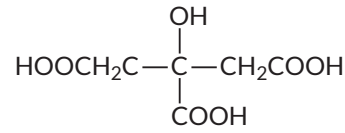
'*A*' while acidification of '*C*' yields carboxylic acid '*D*' with molecular formula of CH_2O_2. Identify the compounds *A*, *B*, *C* and *D* and write all the chemical reactions involved.

OR

(i) Give the IUPAC name of the following compounds:

(a) 

(b) $(CH_3)_2C(OH)COOH$

(c) 

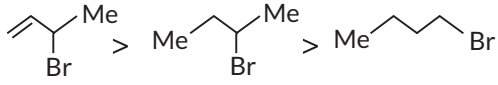
(ii) Write the steps for the following conversions:

(a) Toluene into *p*-nitrobenzoic acid.

(b) 1-Bromopropane into butanoic acid.

Detailed SOLUTIONS

1. (b): S_N1 reaction rate depends upon the stability of the carbocation.



(*B*) (*C*) (*A*)

2. (d): V^{2+} has three unpaired electrons in the *d*-orbitals and shows colour whereas Sc^{3+} and Ti^{4+} have zero and Zn^{2+} has ten electrons in *d*-orbitals and thus are colourless.

3. (c): As the reaction is elementary, sum of stoichiometric coefficients is equal to order of reaction.

$r = k[p_{NO}]^2[p_{O_2}]$

Decreasing volume by $\frac{1}{3}$rd will increase the pressure 3 times.

$r' = k[3p_{NO}]^2\,[3p_{O_2}]$

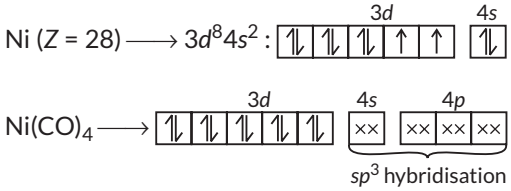
$$\frac{r'}{r}=\frac{k[3p_{NO}]^2[3p_{O_2}]}{k[p_{NO}]^2[p_{O_2}]}=(3)^2(3)=27$$

Rate will increase 27 times.

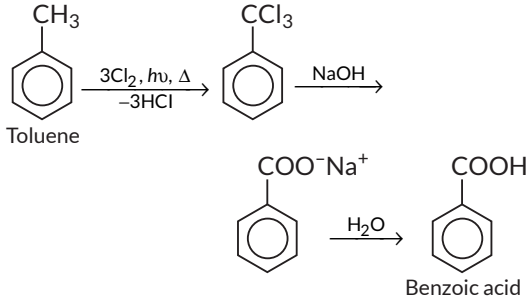
4. (c)

5. (a) : $Ni(CO)_4$ is tetrahedral and diamagnetic due to absence of unpaired electron.

Oxidation state of Ni in $Ni(CO)_4$ = 0

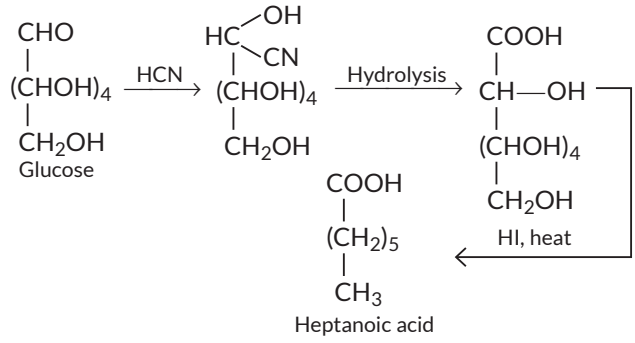


6. (d) :



7. (a)

8. (a):



9. (a) : $CH_3COCl \xrightarrow[\text{(Rosenmund reduction)}]{H_2 - Pd/BaSO_4} CH_3CHO + HCl$

10. (b) : $-\frac{d[H_2]}{dt}=\frac{1}{2}\frac{d[HI]}{dt}=10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1}$

$$\frac{d[HI]}{dt}=2\times10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

11. (b): In an octahedral crystal field, t_{2g} orbitals are lowered in energy by 0.4 Δ_o.

12. (c): Hydroboration-oxidation gives anti– Markownikoff's product.

$$\underset{\text{Propene}}{CH_3-CH=CH_2}\xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ B_2H_6}\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2OH}$$

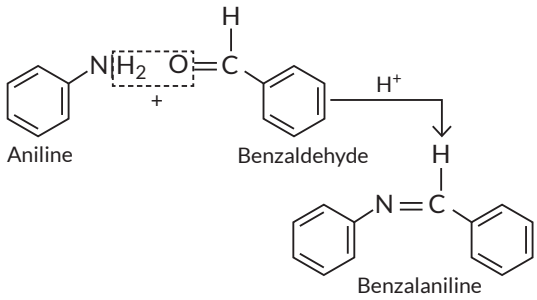
13. (c) : Aliphatic primary amines can be synthesised by Gabriel phthalimide method. Aromatic primary amines cannot be prepared by such method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

14. (b) : The lanthanoid ions are coloured due to the partly filled *f*-orbitals which permit *f* – *f* transitions.

15. (c): Alanine is a non-essential amino acid.

16. (c): Aromatic aldehydes and formaldehyde do not contain α-hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

17. (i) Benzalaniline is formed.



(ii) Primary amine is formed.

$$R—OH + NH_3 \xrightarrow[723\,K]{Al_2O_3} R—NH_2 + H_2O$$

18. (i) For first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

$$= \frac{0.693}{6.93 \times 10^{-3}\,s^{-1}} = 100\ s$$

(ii) For first order reaction, half-life is related to time of 75% completion of reaction by $t_{75} = 2 \times t_{1/2} = 2 \times 100$
$= 200$ s

OR

Difference between the rate of a chemical reaction and the rate constant for the reaction :

Rate of a reaction	Rate constant
The rate of a reaction is variable and is proportional to the concentrations of reactants and to the rate constant.	The rate constant is a constant which depends only on temperature and not on the concentration.

19. (i) Transition metals form a large number of interstitial compounds because small atoms of certain non-metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattice of the transition metals.
(ii) Under the action of light, decomposition of silver bromide takes place in traces where it is illuminated. The number of silver atoms formed is proportional to the quantity of light falling on the surface.

20. Two chiral compounds are possible on monochlorination of 2-methylbutane.

$$CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—CH_2—CH_3 + Cl_2 \xrightarrow{h\upsilon}$$

$$ClCH_2—\overset{*}{C}H(CH_3)—CH_2—CH_3 + CH_3—C(Cl)(CH_3)—CH_2—CH_3$$

(I) (II)

$$+ CH_3—CH(CH_3)—\overset{*}{C}H(Cl)—CH_3 + CH_3—CH(CH_3)—CH_2—CH_2Cl$$

(III) (IV)

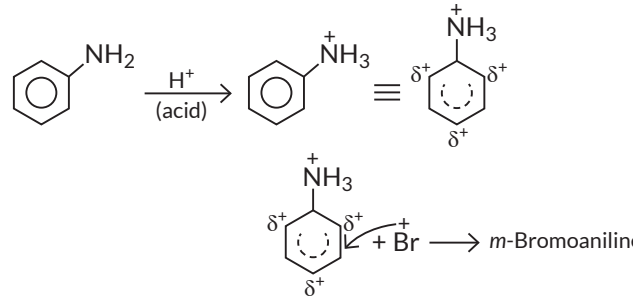
21. The significance of primary structure of proteins is that the amino acid sequence of a protein determines its function and is critical to its biological activity. Even a change of just one amino acid can drastically alter the properties of the entire protein molecule. For example, change of glutamic amino acid by valine amino acid in the protein sequence causes sickle cell anaemia.
Secondary structure of proteins provides mechanical movement of muscles, binds substrates to modify them chemically. Antibody proteins bind foreign proteins.

22. Aqueous NaCl solution ionises as
$NaCl \longrightarrow Na^+ + Cl^-$
Following reactions are possible at cathode,
$2Na^+_{(aq)} + 2e^- \longrightarrow 2Na_{(s)}$; $E° = -2.71$ V
$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$; $E° = -0.83$ V
The reaction with higher $E°$ value will take place, hence H_2 is produced at cathode.
Following reactions may take place at anode,
$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$; $E° = +1.36$ V

$$H_2O_{(l)} \longrightarrow \frac{1}{2}O_{2(g)} + 2H^+ + 2e^-;\ E° = +1.23\ V$$

Due to overvoltage, Cl_2 is liberated at anode.
Hence, the overall reaction is
$2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)} + Cl_{2(g)}$

23. In aniline, $—NH_2$ group is electron releasing, so it directs the incoming electrophile to *ortho* and *para* positions. But in presence of concentrated HCl, aniline forms anilinium ion, in which the $-\overset{+}{N}H_3$ group is electron attracting in nature. So it directs the electrophile (Br^+) to *meta*-position giving *m*-bromoaniline.



24. (i) Molarity is the number of moles of solute dissolved in one litre solution. Molarity decreases with rise in temperature. Molality is the number of moles of solute dissolved in one kilogram solvent and molality is independent of temperature.
(ii) Molality (m) is related to molarity (M) by equation

$$m = \frac{1000M}{(1000\rho - MM_1)}$$

where, M_1 is the molar mass of H_2SO_4

$$m = \frac{1000 \times 18}{(1000 \times 1.8 - 18 \times 98)} = 500 \text{ molal}$$

25. (i) The electronic configuration of Ce ($Z = 58$) is $_{58}Ce = [Xe]\ 4f^1 5d^1 6s^2$
Cerium can lose four electrons ($4f^1 5d^1 6s^2$) in aqueous solution to acquire stable configuration of rare gas xenon. Due to small size and high charge, Ce^{4+} ion has high hydration energy.
(ii) The second and third members in each group of transition elements have very similar atomic radii due to lanthanoid contraction which arises due to poor shielding effect of *f*-electrons.

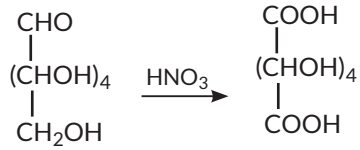
(iii) Any ion of transition elements which possesses unpaired *d*-electrons, (*d-d* transition is possible) shows a characteristic colour.

Ion	Configuration	Ion	Configuration
Cu^+	– $3d^{10}$ (Colourless)	Fe^{2+}	– $3d^6$ (Coloured)
Sc^{3+}	– $3d^0$ (Colourless)	Mn^{2+}	– $3d^5$ (Coloured)
Ti^{4+}	– $3d^0$ (Colourless)	Cr^{3+}	– $3d^3$ (Coloured)

26. (a) Fructopyranose is the sweeter form of fructose. At higher temperatures, the equilibrium shifts towards the less sweet furanose form.

pyranose $\rightleftharpoons$ furanose

(b) On oxidation with nitric acid, glucose yields a dicarboxylic acid, saccharic acid. This indicates presence of one primary (–OH) alcoholic group in glucose because only 1°(–OH) groups are oxidised to (–COOH) group with mild oxidation such as HNO_3 while 2°(–OH) groups need drastic conditions to oxidise. Thus, rest four (–OH) groups in glucose are 2°(–OH) groups.



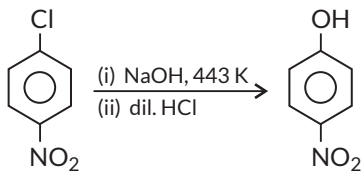
Glucose Saccharic acid

(c) On prolonged heating with HI, glucose gives *n*-hexane which shows it has six carbon atoms in a straight chain.

$CH_2OH(CHOH)_4CHO \xrightarrow[\Delta]{HI}$ $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

Glucose *n*-Hexane

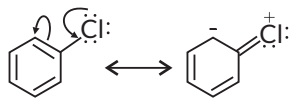
27. (i)



4-Nitrophenol

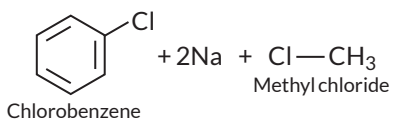
(ii) *Dextro* and *laevo*-rotatory isomers of butan-2-ol are difficult to separate by fractional distillation because they have almost same boiling point.

(iii) In halobenzene C—*X* bond has partial double bond character due to resonance while CH_3—*X* bond is single bond. Thus, bond length of C—*X* bond in halobenzene is smaller than that in CH_3—*X*.

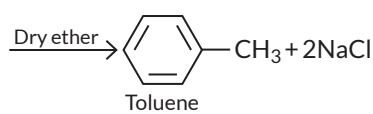


OR

(a)



Chlorobenzene



Toluene

(b) (i) Benzyl chloride gives white precipitate with $AgNO_3$ solution while chlorobenzene does not.

(ii) $CHCl_3$ on reaction with aniline in presence of *alc.* KOH gives foul smelling isocyanide whereas CCl_4 does not.

28. (i) Average rate of reaction between the time interval 30 to 60 seconds is

$$r_{av} = \frac{-[0.17-0.31]}{60-30} = \frac{0.14}{30} = 4.67 \times 10^{-3} \text{ mol L}^{-1}\text{ s}^{-1}$$

(ii) $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

At t = 30 s,

$$k = \frac{2.303}{30}\log\frac{0.55}{0.31} = \frac{2.303}{30}\times 0.249 = 1.91\times10^{-2}\text{s}^{-1}$$

At t = 60 s,

$$k = \frac{2.303}{60}\log\frac{0.55}{0.17} = \frac{2.303}{60}\times 0.5099 = 1.96\times10^{-2}\text{s}^{-1}$$

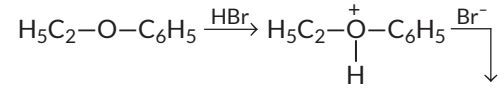
At t = 90 s

$$k = \frac{2.303}{90}\log\frac{0.55}{0.085} = \frac{2.303}{90}\times 0.8109 = 2.07\times10^{-2}\text{ s}^{-1}$$

$\therefore$ Average value of k

$$= \frac{1.91\times10^{-2}+1.96\times10^{-2}+2.07\times10^{-2}}{3} = 1.98\times10^{-2}\text{ s}^{-1}$$

29. (a)



C_2H_5Br + C_6H_5OH

(Bromoethane) (Phenol)

The products formed are bromoethane and phenol.

OR

tert-Butyl iodide and methanol are the products formed on heating *tert*-butylmethyl ether with HI.

(b) $CH_3CH_2OCH_2CH_3 + 2HI \longrightarrow 2CH_3CH_2I + H_2O$

The reaction produces 2 moles of ethyl iodide.

(c) $CH_3-O-CH_2CH_2CH_3 + 2HI \longrightarrow$

Methoxypropane

$CH_3I + CH_3CH_2CH_2I + H_2O$

Methyl iodide Propyl iodide

30. (i) The molality of the given solution is

$$m = \frac{\Delta T_b}{K_b} = \frac{0.60}{5.03} = 0.12 \text{ mol kg}^{-1}$$

(ii) $\Delta T_f = K_f m = 31.8 \times 0.12 = 3.816$ K

(iii) From the molality of the solution, we get

$$\text{Molality} = \frac{n_2\times1000}{m_1} = \frac{m_2/M_2\times1000}{m_1}$$

or $0.12 = \frac{3/M_2\times1000}{100}$; $M_2 = 250 \text{ g mol}^{-1}$

OR

$$\pi = CRT = \frac{n_2}{V}RT;\ n_2 = \frac{m_2}{M_2} = \frac{3}{250} = 0.012$$

$$V = \frac{\text{Mass of solution}}{\text{Density of solution}} = \frac{100+3}{1.64} = 62.8\ \text{cm}^3 = 0.0628\ \text{dm}^3$$

Hence, $\pi = \dfrac{0.012 \times 0.082 \times 298}{0.0628} = 4.669$ atm

31. (a) Anhydrous $CuSO_4$ has no ligand. So, crystal field splitting does not occur so, it does not show any colour but in hydrated form it is linked with H_2O ligand so, it shows colour due to *d-d* transition.

(b) $[Co(NH_3)_6]Cl_3 > [Co(NH_3)_5\ Cl]Cl_2 > [Co(NH_3)_4Cl_2]Cl > [Co(NH_3)_3Cl_3]$

As the number of ions produced increases, conductivity increases.

(c) Pentaamminenitrito-N-cobalt(III) cation : $[Co(NO_2)(NH_3)_5]^{2+}$

(d) $[Ti(H_2O)_6]Cl_3$ is a complex compound. In presence of 6 H_2O molecules the *d*-orbitals of Ti^{3+} undergo splitting. The compound is coloured (violet) due to *d-d* transition. On heating water molecules escape, *d*-orbitals become degenerate. There is no *d-d* transition. Hence, compound becomes colourless.

(e) Geometrical isomerism is not possible in tetrahedral complexes because the ligands are equidistant. *i.e.*, relative positions of the ligands attached to the central metal atom is same with respect to each other.

(f) IUPAC name : [Chlorido*bis*(ethane-1,2-diamine) nitrito-O-cobalt(III) ion].

Shape : Octahedral

(g) EDTA (ethylenediamine tetraacetate) is used for the estimation of Mg^{2+} and Ca^{2+} ions present in hard water.

32. (a) $\kappa = 1.29 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$

$\kappa = \dfrac{1}{R} \times$ Cell constant

$\Rightarrow$ Cell constant $= \kappa \times R$

$= 1.29\ \text{S m}^{-1} \times 85\ \text{S}^{-1} = 109.65\ \text{m}^{-1}$

For second solution,

$$\kappa = \frac{1}{R} \times \text{Cell constant} = \frac{1}{96\ \Omega} \times 109.65\ \text{m}^{-1} = 1.142\ \Omega^{-1}\text{m}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142\ \Omega^{-1}\text{m}^{-1} \times 1000\ \text{cm}^3}{0.052\ \text{mol}}$$

$$\Lambda_m = \frac{1.142\ \Omega^{-1}\text{cm}^{-1} \times 10^{-2} \times 1000\ \text{cm}^3}{0.052\ \text{mol}}$$

$= 219.61\ \text{S cm}^2\ \text{mol}^{-1}$

(b) $$\Lambda_m^c = \frac{\kappa \times 1000}{C} = \frac{(7.896 \times 10^{-5}) \times 1000}{0.00241}$$

$= 32.76\ \text{S cm}^2\ \text{mol}^{-1}$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1-(8.4 \times 10^{-2})}$$

$= 1.86 \times 10^{-5}$

OR

(a) $\Delta G^\circ = -nFE^\circ_{cell}$

$$E^\circ_{cell} = \frac{\Delta G^\circ}{-nF} = \frac{-43600}{-2 \times 96500} = 0.226\ \text{V}$$

$2AgCl_{(s)} + H_{2(g)}(1\ \text{atm}) \longrightarrow 2Ag_{(s)} + 2H^+(0.1\ \text{M}) + 2Cl^-(0.1\ \text{M})$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= 0.226 - \frac{0.0591}{2} \log \frac{(0.1)^2}{(1)} = 0.226 - \frac{0.0591}{2} \log (10^{-2})$$

$$= 0.226 - \frac{0.0591}{2} \times (-2) = 0.226 + 0.0591 = 0.2851\ \text{V}$$

(b) (i) $2H^+ + 2e^- \rightarrow H_2\uparrow$ (Cathode)

$2Cl^- \rightarrow Cl_2 + 2e^-$ (Anode)

(ii) $2H^+ + 2e^- \rightarrow H_2\uparrow$ (Cathode)

$2Br^- \rightarrow Br_2 + 2e^-$ (Anode)

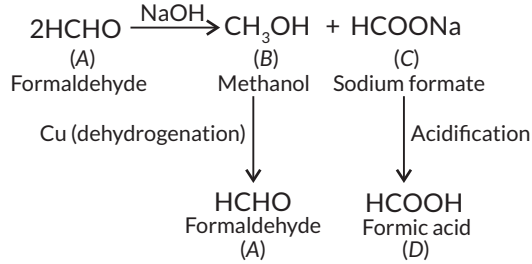
(iii) The electrolysis of $NaF_{(aq.)}$ leads only to the reduction and oxidation of H_2O. The $NaF_{(aq.)}$ serves only as an electrolyte to allow the electricity to be conducted through the electrolytic cell.

$2H^+ + 2e^- \rightarrow H_2\uparrow$ (Cathode)

$2OH^- \rightarrow H_2O + \frac{1}{2} O_2 + 2e^-$ (Anode)

33. Since, the molecular formula of *D* is CH_2O_2, thus, *D* is HCOOH (formic acid). *D* is obtained by the acidification of *C*, so, *C* is sodium formate (HCOONa).

Thus, *A* must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base).



Thus, *A* = Formaldehyde (HCHO)

B = Methanol (CH_3OH)

C = Sodium formate (HCOONa)

D = Formic acid (HCOOH)

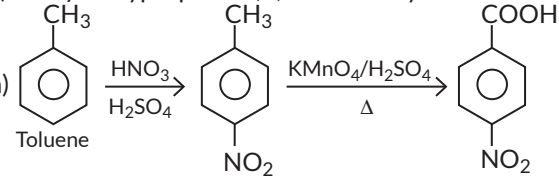
OR

(i) (a) 2-Cyclohexylacetic acid

(b) 2-Hydroxy-2-methylpropanoic acid

(c) 2-Hydroxypropane-1,2,3-tricarboxylic acid

(ii) (a)



p-Nitrobenzoic acid

(b) $CH_3CH_2CH_2Br \xrightarrow[\text{Ether}]{Mg} CH_3CH_2CH_2MgBr \xrightarrow[H^+]{CO_2} CH_3CH_2CH_2COOH$

1-Bromopropane — Butanoic acid

PRACTICE PAPER 3

General Instructions :

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple - choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case - based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. The formula of the complex potassium trichlorido-ethylene platinate(II) is
   (a) $K[PtCl_3(C_2H_4)]$ (b) $K_2[PtCl_3(C_2H_4)_3]$
   (c) $K_4[PtCl_3(C_2H_4)]$ (d) $K_3[Pt_2Cl_3(C_2H_4)_3]$

2. *n*-Propyl alcohol and *iso*-Propyl alcohol can be chemically distinguished by which reagent?
   (a) PCl_5 (b) H_2/Ni
   (c) $K_2Cr_2O_7/H_2SO_4$ (d) $O_3/Zn\text{-}H_2O$

3. The anomeric carbon in *D* (+) glucose is
   (a) C-1 carbon (b) C-2 carbon
   (c) C-5 carbon (d) C-6 carbon.

4. If an equimolar solution of $CaCl_2$ and $AlCl_3$ in water have boiling point of T_1 and T_2 respectively then
   (a) $T_1 > T_2$ (b) $T_2 > T_1$ (c) $T_1 = T_2$ (d) $T_1 \neq T_2$

5. The order of polarity of CH_3I, CH_3Br and CH_3Cl molecules follows the order
   (a) $CH_3Br > CH_3Cl > CH_3I$
   (b) $CH_3I > CH_3Br > CH_3Cl$
   (c) $CH_3Cl > CH_3Br > CH_3I$
   (d) $CH_3Cl > CH_3I > CH_3Br$

6. Specific conductance of 0.1 M NaCl solution is 1.01×10^{-2} ohm^{-1} cm^{-1}. Its molar conductance in ohm^{-1} cm^2 mol^{-1} is
   (a) 1.01×10^2 (b) 1.01×10^3
   (c) 1.01×10^4 (d) 1.01

7. What is the colour of the end product 'Y' of the following set of reactions?

   Phenol + Phthalic anhydride $\xrightarrow[\Delta]{\text{conc. } H_2SO_4} X \xrightarrow{NaOH} Y$

   (a) Green (b) Blue (c) Pink (d) Yellow

8. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following :
   (a) Mn_2O_7 (b) MnO_2 (c) $MnSO_4$ (d) Mn_2O_3

9. Which is a high spin complex?
   (a) $[CoF_6]^{3-}$ (b) $[Fe(CN)_6]^{3-}$
   (c) $[Fe(CN)_6]^{4-}$ (d) None of these

10. If rate constant is numerically same for three reactions of first, second and third order, then which of the following is correct?
    (a) If $[A] = 1$ then $r_1 = r_2 = r_3$
    (b) If $[A] > 1$ then $r_1 > r_2 > r_3$
    (c) If $[A] < 1$ then $r_1 < r_2 < r_3$
    (d) All of the above.

11. Reaction by which benzaldehyde cannot be prepared?
    (a) + CO + HCl in presence of anhydrous $AlCl_3$
    (b) + Zn/Hg and conc. HCl
    (c) + CrO_2Cl_2 in CS_2 followed by H_3O^+
    (d) + H_2 in presence of Pd-$BaSO_4$

12. Aniline on heating with conc. HNO_3 + conc. H_2SO_4 mixture yields
    (a) *o*- nitroaniline (b) *m*-nitroaniline
    (c) *p*-nitroaniline (d) all of these.

13. Given below are two statements labelled as Assertion (A) and Reason (R).

    Assertion (A) : Hydroxylation of ethylene with Baeyer's reagent gives ethylene glycol.

Reason (R) : Baeyer's reagent is $H_2O_2 + FeSO_4$.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

14. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion : If 0.1 M NaCl solution boils at 101°C, then 0.1 M $BaCl_2$ solution will boil at approximately 101.5 °C.

Reason : $BaCl_2$ has higher molecular mass than NaCl.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

15. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A) : Ce^{4+} is used as an oxidising agent in volumetric analysis.

Reason (R) : Ce^{4+} has the tendency of attaining +3 oxidation state.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion : DNA has a double helix structure.

Reason : The two strands in a DNA molecule are exactly similar.

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION-B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. Give reasons :

(i) Racemic mixture is optically inactive.
(ii) The presence of nitro group ($-NO_2$) at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

18. The rate constant for decomposition of N_2O_5 is 3.0×10^{-5} s^{-1}. If the rate of the reaction is 2.40×10^{-5} mol L^{-1} s^{-1}, find the concentration of N_2O_5 in mol L^{-1}.

19. Name the products with chemical reactions when ethanamine reacts with following compounds.

(i) $CHCl_3$ + *alc.* KOH
(ii) C_6H_5COCl

OR

How will you convert aniline to

(i) *N*-methylaniline
(ii) acetanilide?

20. Two solutes *X* and *Y* in equal amounts are dissolved separately in 10 moles of solvent *C*. If *X* molecule is heavier than *Y* molecule, which solution will have larger relative lowering of vapour pressure?

21. (i) Write down the IUPAC name of the following complex :
$[Cr(NH_3)_2Cl_2(en)]Cl$ (*en* = ethylenediamine)
(ii) Write the formula for the following complex :
Pentaamminenitrito-O-cobalt(III).

SECTION-C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. Give reasons for of the following observations.

(i) Aromatic 1° amines cannot be prepared by Gabriel phthalimide reaction. Explain.
(ii) Select the amine which is most reactive towards dil. HCl among the following :
CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$
(iii) Boiling points of amines are less than the alcohols of similar molecular mass. Why?

23. Write chemical equations and reaction conditions for the conversion of

(a) Chlorobenzene to phenol
(b) Propene to 1-bromopropane
(c) Chlorobenzene to toluene.

OR

Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.

(a) 1-Bromo-1-methylcyclohexane
(b) 2-Chloro-2-methylbutane

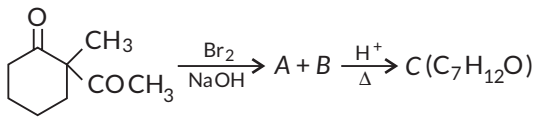
24. (a) Write the Nernst equation.
(b) Calculate the emf of the following cells at 298 K :
$Fe_{(s)} | Fe^{2+}(0.001\ M) || H^+(1\ M) | H_{2(g)}(1\ bar) | Pt_{(s)}$
[Given : $E°_{Fe^{2+}/Fe} = -0.44\ V$]

25. How are the following conversions carried out?
(i) Phenol to toluene
(ii) Ethanol to butane
(iii) Propene to propan-2-ol

26. (i) A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is added to this solution, the new vapour pressure becomes 2.9 kPa at 298 K. Calculate
(a) vapour pressure of water at 298 K and
(b) the molecular mass of solute.
(ii) 1.22 g of benzoic acid is dissolved in 100 g of acetone (K_b for acetone = 1.7 K kg mol^{-1}) and 100 g of benzene (K_b = 2.6 K kg mol^{-1}).
The elevations in boiling points ΔT_b is 0.17 °C and 0.13 °C respectively. What are molar masses of benzoic acid in these two solvents?

27. Write the IUPAC name of the given complex along with its hybridisation and structure.
$K_2[Cr(NO)(NH_3)(CN)_4]$, μ = 1.73 B.M.

28. Identify *A*, *B* and *C* and give their structures.

(a) 

(b) Write the equations involved in the following reactions :
(i) Stephen reaction (ii) Etard reaction

SECTION-D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

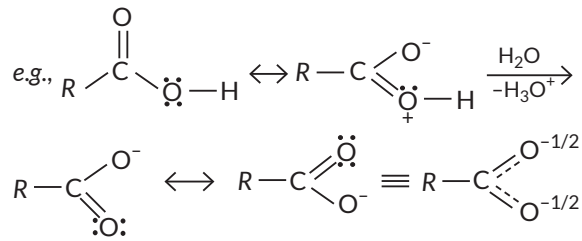
29. The rate of a chemical reaction is the change in the concentration of any one of the reactants or products per unit time.
The thermal decomposition of N_2O_5 occurs as : $2N_2O_5 \rightarrow 4NO_2 + O_2$
Experimental studies suggest that rate of decomposition of N_2O_5, rate of formation of NO_2 or rate of formation of O_2 all becomes double if concentration of N_2O_5 is doubled.

Answer the following questions :
(a) Write the mechanism for decomposition of N_2O_5.
(b) Write the rate of decomposition of N_2O_5.
(c) For the given reaction,
*R*Cl + NaOH → *R*OH + NaCl
What will be the new rate of reaction when concentration of *R*Cl is reduced to half?

OR

If conc. of reactant is doubled for a first order reaction, then what will be the rate of reaction and rate constant?

30. Carboxylic acids dissociate in water to give carboxylate ion and hydronium ion.
$RCOOH + H_2O \longrightarrow RCOO^- + H_3O^+$
The acidity of carboxyl group is due to the presence of positive charge on oxygen which liberates proton. The carboxylate ion formed is resonance stabilised.



Carboxylic acids are stronger acids than phenols. Electron withdrawing groups (EWG) increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of negative charge by inductive and/or resonance effects. Electron donating groups (EDG) decrease the acidity by destabilising the conjugate base.

Answer the following questions :
(a) Give one reaction showing the acidic property of carboxylic acid.

OR

Write the correct order of acidic strength for following acids.
$CF_3COOH, CHCl_2COOH, HCOOH, CH_3COOH$
(b) Carboxylic acids are more acidic than phenols. Why?
(c) (i) Among the following acids, which acid has smallest dissociation constant?
$CH_3CH(F)COOH, FCH_2CH_2COOH,$
$BrCH_2CH_2COOH, CH_3CH(Br)COOH$
(ii) Arrange the following in the increasing order of their boiling points.
$CH_3CHO, CH_3COOH, CH_3CH_2OH$

SECTION-E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt **any five** of the following.
(a) What is the basic structural difference between starch and cellulose?
(b) Give an example of anomers.

(c) Write the products of the following reaction :

$$\text{Sucrose} \xrightarrow{H^+} A + B$$

(d) What is invert sugar?

(e) What are monosaccharides?

(f) What are the hydrolysis products of :
(a) sucrose (b) lactose?

(g) What happens when *D*-glucose is treated with:
(a) HI (b) HNO_3?

32. (a) Write chemical equations for the conversion of
(i) chromite ore to sodium chromate
(ii) pyrolusite to potassium manganate
(iii) potassium permanganate to manganese dioxide.

(b) What is lanthanide contraction? Discuss its cause.

OR

How would you account for the following :
(i) Mn^{3+} is a good oxidising agent.
(ii) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.
(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.
(iv) Cr^{2+} is a stronger reducing agent than Fe^{2+}.
(v) The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic.

33. A cell is prepared by dipping a copper rod in 0.01 M copper sulphate solution, and zinc rod in 0.02 M zinc sulphate solution. The standard reduction potentials of copper and zinc are +0.34 V and –0.76 V respectively.

(a) What will be the cell reaction?

(b) How will the cell be represented?

(c) What will be the emf of the cell?

OR

For the standard cell, $Cu_{(s)} | Cu^{2+}_{(aq)} || Ag^{+}_{(aq)} | Ag_{(s)}$

Given: $E°_{Cu^{2+}/Cu} = 0.34$ V, $E°_{Ag^{+}/Ag} = 0.80$ V

(a) Identify cathode and anode as the current is drawn through the cell.

(b) Write the reactions taking place at the electrodes.

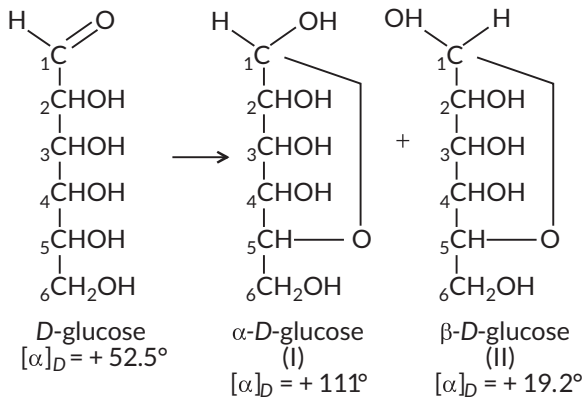
(c) Calculate the standard electrode potential.

Detailed SOLUTIONS

1. (a)

2. (c): Primary alcohol on oxidation with potassium dichromate gives an aldehyde while secondary alcohol gives a ketone.

3. (a): *D*-glucose exists in two optically active forms known as α-*D*-glucose and β-*D*-glucose. The two isomers are inter convertible in aqueous solution.



D-glucose $[\alpha]_D = +52.5°$ | α-*D*-glucose (I) $[\alpha]_D = +111°$ | β-*D*-glucose (II) $[\alpha]_D = +19.2°$

Carbon-1 in both configurations I and II is called an anomeric carbon atom.

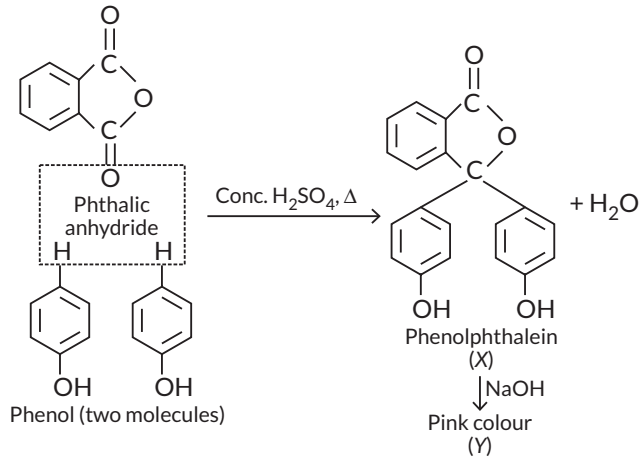
4. (b): Since, number of particles of $AlCl_3$ in solution is more than that of $CaCl_2$, ΔT_b of $AlCl_3$ is more. Hence, boiling point of $AlCl_3$ solution is higher.

5. (c): Since, the electronegativity follows the order Cl > Br > I, the order of polarity is $CH_3Cl > CH_3Br > CH_3I$.

6. (a): $\Lambda_m = \dfrac{\kappa \times 1000}{M} = \dfrac{1.01 \times 10^{-2} \times 1000}{0.1}$

$= 1.01 \times 10^2\ \Omega^{-1}\ cm^2\ mol^{-1}$

7. (c): The product '*X*' is phenolphthalein that gives pink colour with NaOH.



8. (a): $2KMnO_4 + 2H_2SO_4(conc.) \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$ (green oily)

9. (a): F^- being weak field ligand results in high spin complex.

10. (a): Rate law for first order, $r_1 = k[A]^1$
For second order, $r_2 = k[A]^2$
For third order, $r_3 = k[A]^3$

Then we can say,
If $[A] = 1$; $r_1 = r_2 = r_3$
If $[A] < 1$ then $r_1 > r_2 > r_3$
If $[A] > 1$ then $r_3 > r_2 > r_1$

11. (b): Reduction in presence of Zn-Hg and conc. HCl is useful for aldehyde and ketone but carboxylic acid group remains unaffected.

12. (d): Aniline on heating with conc. HNO_3 and conc. H_2SO_4 mixture yields *o*-nitroaniline (2%), *p*-nitroaniline (51%) and *m*-nitroaniline (47%).

13. (c): Baeyer's reagent is 1% alkaline solution of $KMnO_4$.

14. (b): 0.1 M NaCl = 0.2 M Na^+ and Cl^- ions ; 0.1 M $BaCl_2$ = 0.3 M Ba^{2+} and Cl^- ions. Thus, concentration of Ba^{2+} and Cl^- ions is 1.5 times of concentration of Na^+ and Cl^- ions. Hence, elevation in boiling point will be 1.5 times.

15. (a): The element which can reduce itself acts as an oxidising agent.

16. (c): The two strands in a DNA molecule are not exactly similar but are complimentary.

17. (i) Racemic mixture contains equal amount of *d*- and *l*-forms, hence due to optical rotation one enantiomer is cancelled by another.
(ii) The presence of nitro group at *o*-and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

18. $2N_2O_5 \longrightarrow 4NO_2 + O_2$
Rate = $k[N_2O_5]$
$\therefore \quad 2.40 \times 10^{-5} = 3.0 \times 10^{-5}\,[N_2O_5]$

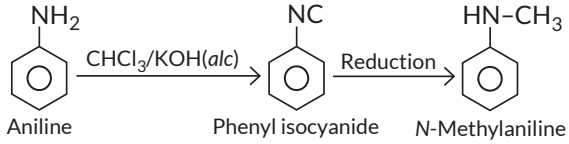
$$[N_2O_5] = \frac{2.40\times10^{-5}}{3.0\times10^{-5}} = 0.8$$

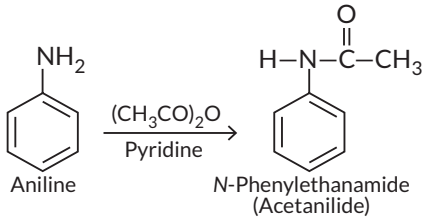
Concentration of N_2O_5 is 0.8 mol L^{-1}.

19. (i) $CH_3CH_2NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} CH_3CH_2NC + 3KCl + 3H_2O$

(ii) $CH_3CH_2NH_2 + C_6H_5COCl \longrightarrow CH_3CH_2NHCOC_6H_5 + HCl$

OR

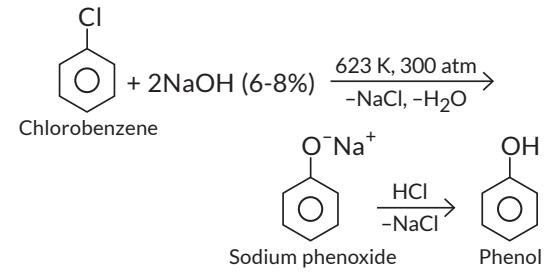
(i) 

(ii) 

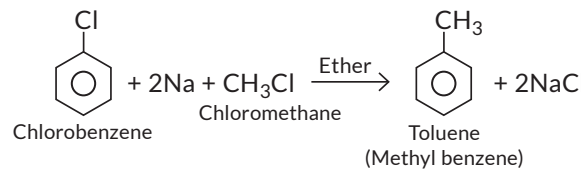
20. Molar mass of *Y* is less than that of *X*, therefore, for the same mass of *X* and *Y*, moles of *Y* will be more than the moles of *X*. Thus, mole fraction of *Y* will be more than that of *X*. Hence, relative lowering of vapour pressure will be larger in case of *Y*.

21. (i) Diamminedichlorido(ethane-1, 2-diamine) chromium(III) chloride.
(ii) $[Co(NH_3)_5(ONO)]^{2+}$

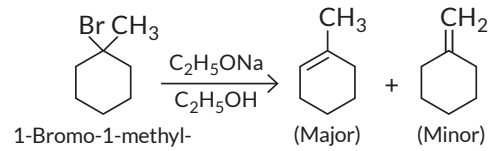
22. (i) Aromatic 1° amines cannot be prepared by Gabriel phthalimide reaction because aryl halides do not undergo nucleophilic substitution reactions with potassium phthalimide under mild conditions.
(ii) $(CH_3)_2NH$ is most basic amongst the given amines. Thus, it is most reactive amine towards HCl.
(iii) Amines are less polar than alcohols because electronegativity difference between N–H is less than that of O–H. Intermolecular H-bond in amines is weaker than that in alcohols.

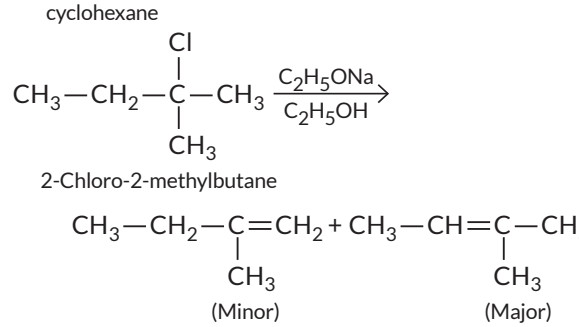
23. (a) 

(b) $CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br$
Propene 1-Bromopropane

(c) 

OR

(a) 

(b) 

24. (a) For the equation,
$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF}\log\frac{1}{\left[M^{n+}_{(aq)}\right]}$$

$$= E^{\circ}_{cell} - \frac{0.059}{n}\log\frac{1}{\left[M^{n+}_{(aq)}\right]}$$

Concentration of solids is taken as unity.

(b) $Fe_{(s)} \mid Fe^{2+}(0.001\ M) \parallel H^{+}(1\ M) \mid H_{2(g)}(1\ bar) \mid Pt_{(s)}$

At anode : $Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^{-}$

At cathode : $2H^{+}_{(aq)} + 2e^{-} \longrightarrow H_{2(g)}$

Cell reaction : $Fe_{(s)} + 2H^{+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$

$\therefore \quad n = 2$

Using Nernst equation at 298 K,

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]\times p_{H_2}}{[H^{+}]^2}$$

For the given cell,

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{H^{+}/H_2} - E^{\circ}_{Fe^{2+}/Fe}$

$= 0 - (-0.44) = +0.44$ V

Given : $[Fe^{2+}] = 0.001$ M; $[H^{+}] = 1$ M; $p_{H_2} = 1$ bar

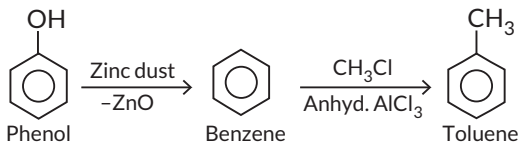
Putting values in Nernst equation,

$$E_{cell} = 0.44 - 0.0295\log\frac{0.001\times 1}{1^2}$$

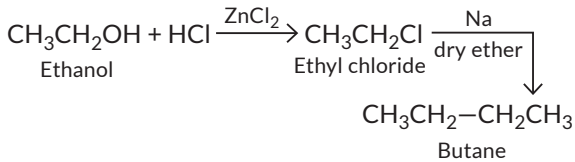
$= 0.44 - 0.0295 \log 10^{-3} = 0.44 - [(0.0295) \times (-3)]$

$= 0.44 + 0.0885 = 0.53$ V

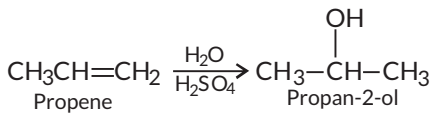
26. (i)



(ii)



(iii)



26. (i) (a) The relative lowering of vapour pressure is given by the following expression,

$(p^{\circ}_{solvent} - p_{solution})/p^{\circ}_{solvent} = n_2/(n_1 + n_2)$

for dilute solutions, $n_2 << n_1$, therefore

$(p^{\circ}_{solvent} - p_{solution})/p^{\circ}_{solvent} = n_2/n_1$

$= (W_2 \times M_1)/(M_2 \times W_1)$

$(p^{\circ}_{solvent} - 2.8)/p^{\circ}_{solvent} = (30 \times 18)/(M_2 \times 90)$

$(p^{\circ}_{solvent} - 2.8)/p^{\circ}_{solvent} = 6/M_2$ ...(1)

Similarly for second case we get,

$(p^{\circ}_{solvent} - 2.9)/p^{\circ}_{solvent} = (30 \times 18)/(M_2 \times 108)$

$(p^{\circ}_{solvent} - 2.9)/p^{\circ}_{solvent} = 5/M_2$ ...(2)

On solving eq. (1) and (2), we get

$(p^{\circ}_{solvent} - 2.8)/(p^{\circ}_{solvent} - 2.9) = 6/5$

$\therefore \quad p^{\circ}_{solvent} = 3.4$ kPa

i.e., vapour pressure of water at 298 K is 3.4 kPa

(b) Substituting the value of $p^{\circ}_{solvent}$ in (1) we get,

$(3.4 - 2.8)/3.4 = 6/M_2$ or $0.6/3.4 = 6/M_2$

$\therefore \quad M_2 = 34$ g

(ii) $\Delta T_b = K_b m = K_b \dfrac{w_B}{M_B \times w_A \text{ (in kg)}}$

Let molar mass of benzoic acid be M_B and M'_B in acetone and benzene respectively.

In acetone,

$$0.17 = \frac{1.7\times 1.22\times 1000}{M_B \times 100} \Rightarrow M_B = 122\ g\ mol^{-1}$$

In benzene, $0.13 = \dfrac{2.6\times 1.22\times 1000}{M'_B \times 100}$

$$M'_B = \frac{2.6\times 1.22\times 1000}{0.13\times 100} = 244\ g\ mol^{-1}$$

27. The spin magnetic moment (μ) of complex = 1.73 B.M.

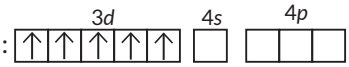
$\sqrt{n(n+2)} = 1.73$ B.M. or $n \simeq 1$

This indicates that in the complex, chromium has one unpaired electron *i.e.*, Cr^{+}. Thus, the ligand NO is unipositively charged.

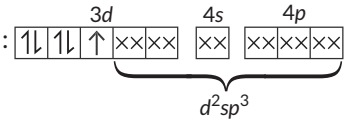
IUPAC name :

Potassium amminetetracyanonitrosoniumchromate(I).

$[Cr^{+}]$:

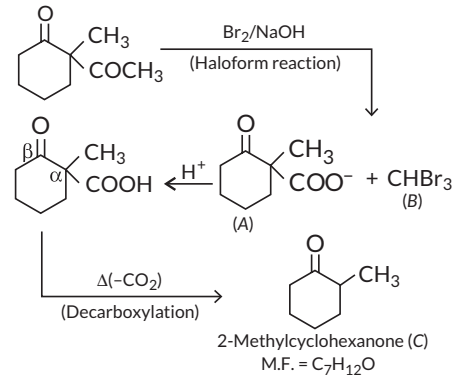


Cr^{+} in complex :

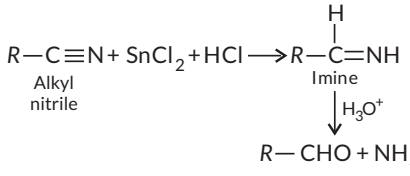


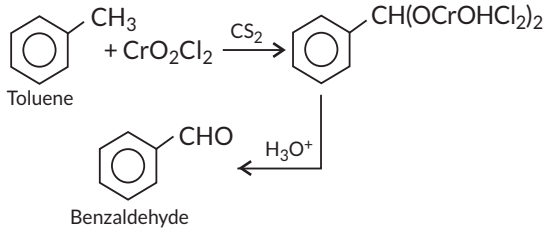
Hybridisation = d^2sp^3, Shape = Octahedral

28. (a)



(i)



(ii) 

29. (a) $N_2O_5 \xrightarrow{Slow} NO_2 + NO_3$

$N_2O_5 + NO_3 \xrightarrow{Fast} 3NO_2 + O_2$

(b) $\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$

(c) For the given reaction, rate of reaction (r) = $k[RCl]$ (where, k is rate constant). Therefore, if the concentration of [RCl] is reduced to half, then new rate $(r') = \frac{k}{2}[RCl]$.

OR

For first order reaction, $Rate_1 = k[A_1]$

According to question, $[A_2] = [2A_1]$

$\therefore$ $Rate_2 = k[2A_1] \Rightarrow Rate_2 = 2\ Rate_1$

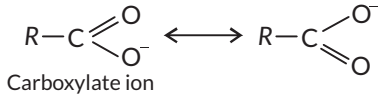
For a given reaction, rate constant is constant and independent of the concentration of reactant.

30. (a) $2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2\uparrow$

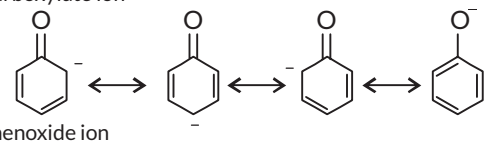
OR

$CF_3COOH > CHCl_2COOH > HCOOH > CH_3COOH$

(b) The higher acidity of carboxylic acid as compared to phenol is due to stabilisation of carboxylate ion by two resonance structure in which –ve charge is at more electronegative oxygen. But in resonance of phenoxide ion the –ve charge is at less electronegative carbon atom. So, resonance in phenoxide ion is less stable as compared to carboxylate ion.

(i) 

Carboxylate ion

(ii) 

Phenoxide ion

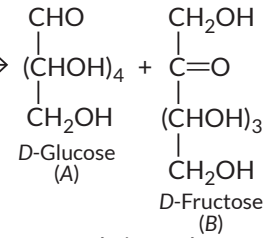
(c) (i) $BrCH_2CH_2COOH$ is least acidic or has less K_a *i.e.* less dissociation constant.

(ii) Increasing order of boiling point :

$CH_3CHO < C_2H_5OH < CH_3COOH$

31. (a) Starch consists of two components, *i.e.*, amylose and amylopectin. Amylose is a linear polymer of α-*D*-(+) glucose in which C_1 of one glucose unit is connected to C_4 of the other glucose unit through α-glycosidic linkage. Amylopectin has similar structure but it has branched chain structure. Chain is formed by C_1-C_4 glycosidic linkage and branching occurs by C_1-C_6 glycosidic linkage. Cellulose, on the other hand, is a straight chain polysaccharide composed of β-*D*-glucose and the monomeric glucose units are linked together by C_1 – C_4 β-glycosidic linkage.

(b) α-*D*(+)-glucose and β-*D*(+)-glucose.

(c) Sucrose $\xrightarrow{H^+}$ 

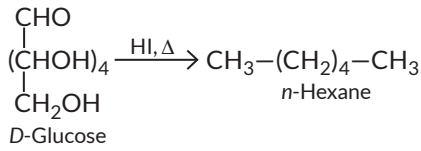
D-Glucose (*A*) + *D*-Fructose (*B*)

(d) Hydrolysis of sucrose brings about a change in the sign of rotation, from *dextro*(+) to *laevo*(–) and the product is known as invert sugar.

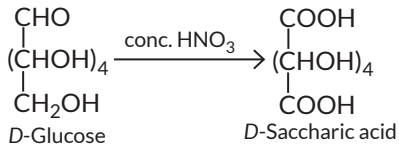
(e) Carbohydrates which cannot be further hydrolysed to give simple units of polyhydroxy aldehydes or ketones are known as monosaccharides.

(f) (a) Sucrose on hydrolysis yields equimolar ratio of *D*(+)-glucose and *D*(–)-fructose.

(b) Lactose on hydrolysis gives β-*D*-(+)-glucose and β-*D*-(+)-galactose in equimolar ratio.

(g) (a) 

D-Glucose → *n*-Hexane

(b) 

D-Glucose → *D*-Saccharic acid

32. (a) (i) $4FeCr_2O_7 + 8Na_2CO_3 + 7O_2 \xrightarrow{heat}$ $8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

Chromite ore → Sodium chromate

(ii) $2MnO_2 + 4KOH + O_2 \xrightarrow{heat} 2K_2MnO_4 + 2H_2O$

Pyrolusite → Potassium manganate

(iii) $2KMnO_4 \xrightarrow{\Delta} MnO_2 + K_2MnO_4 + O_2$

Potassium permanganate → Manganese dioxide

(b) The steady decrease in atomic and ionic radii of lanthanides as we move from La to Lu, is known as lanthanide contraction.

Cause : In lanthanides, last electron enters the 4*f* sub-shell *i.e.*, second last shell. The shape of *f*-orbitals is very much diffused, because of this reason the mutual shielding of 4*f*-electrons is very little. The nuclear charge increases at each step due to the increase in atomic number, while the mutual shielding effect of 4*f*-electrons is comparatively negligible. This causes a decrease in size of the 4*f* sub-shell with the increase in atomic number.

OR

(i) Mn^{2+} is more stable due to half-filled d^5 configuration and Mn^{3+} easily changes to Mn^{2+} hence, it is a good oxidising agent.

(ii) Mn^{2+} has half filled d^5 stable configuration. Hence Mn^{3+} reduces easily to Mn^{2+}. This explains the more positive value of $E°_{Mn^{3+}/Mn^{2+}}$.

(iii) Both fluorine and oxygen have small size, high electronegativity and high negative electron gain enthalpy. Hence, they can oxidise a metal to their highest oxidation state.

(iv) Cr^{2+} is a stronger reducing agent than Fe^{2+}. $E°_{Cr^{3+}/Cr^{2+}}$ is negative (−0.41 V) whereas $E°_{Fe^{3+}/Fe^{2+}}$ is positive (+ 0.77 V). Thus Cr^{2+} is easily oxidised to Cr^{3+} but Fe^{2+} cannot be easily oxidised to Fe^{3+}. Hence, Cr^{2+} is stronger reducing agent than Fe^{2+}.

(v) Compounds of transition metals with lowest oxidation states are basic due to their ability to get oxidised to higher oxidation states. Whereas, the higher oxidation state of metal and compounds gets reduced to lower ones and hence acts as acidic in nature.

33. (a) $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(b) The cell can be represented as

$Zn_{(s)}|Zn^{2+}_{(aq)}$ (0.02 M)||$Cu^{2+}_{(aq)}$ (0.01 M)|$Cu_{(s)}$

(c) $E°_{cell} = E_{cathode} - E_{onode}$

$= 0.34 - 0.76 = 1.10$ V

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10 - \frac{0.059}{2}\log\frac{0.02}{0.01}$$

$= 1.10 - 0.0088$

$= + 1.091$ V

OR

(a) Silver electrode will act as cathode because its electrode potential is higher than copper, while the copper will act as anode.

(b) At anode : $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$

At cathode : $2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$

Overall : $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

(c) $E°_{cell} = E°_{cathode} - E°_{anode} = 0.80 - 0.34 = 0.46$ V

PRACTICE PAPER 4

General Instructions :

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple - choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case - based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. The expression to calculate time required for completion of zero order reaction is

(a) $t = \frac{[R]_o}{k}$ (b) $t = [R] - [R]_o$

(c) $t = \frac{k}{[R]_o}$ (d) $t = \frac{[R]_0 - [R]}{[R]_o}$

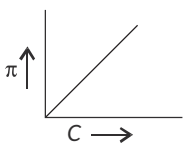
2. In the given reaction, product '*A*' is

$$CH_3CCl_2CH_3 \xrightarrow[NaOH]{H_2O} \text{'}A\text{'}$$

(a) CH_3CH_2CHO (b) CH_3CH_2OH
(c) CH_3COCH_3 (d) CH_3CHO

3. A graph showing variation of osmotic pressure (π) versus molar concentration (C) of an aqueous solution at temperature T is given.

The slope of the line represents



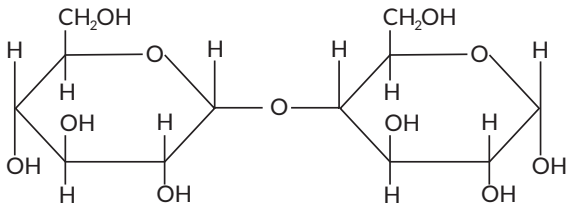
(a) solution constant R
(b) absolute temperature T
(c) RT
(d) degree of ionisation.

4. The crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complexes is related as

(a) $\Delta_t = \frac{2}{9}\Delta_o$ (b) $\Delta_t = \frac{5}{9}\Delta_o$

(c) $\Delta_t = \frac{4}{9}\Delta_o$ (d) $\Delta_t = 2\,\Delta_o$

5. Study the structure of maltose and mark the incorrect statement.



(a) Maltose is composed of two α-D-glucose units.
(b) C-1 of one glucose is linked to C-4 of other unit.
(c) It is a non-reducing sugar.
(d) It is a disaccharide.

6. A solution contains Pb^{2+} and Fe^{2+} ions. To it some quantity of Fe and Pb is added. Then

$[E^\circ_{Fe^{2+}/Fe} = -0.44\ V,\ E^\circ_{Pb^{2+}/Pb} = -0.126\ V]$

(a) concentration of Pb^{2+} ions will remain unaffected
(b) concentration of Pb^{2+} ions will increase
(c) concentration of Fe^{2+} ions will increase
(d) concentration of Fe^{2+} ions will decrease.

7. The Wurtz-Fittig reaction involves condensation of

(a) two molecules of aryl halides
(b) one molecule of aryl-halide and one molecule of alkyl halide
(c) one molecule of aryl halide and one molecule of phenol
(d) two molecules of alkyl halides.

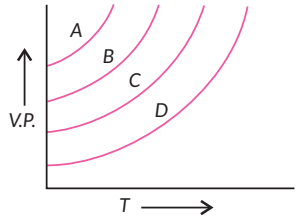
8. A first order reaction takes 40 min for 30% decomposition. What will be $t_{1/2}$?

(a) 77.7 min (b) 52.5 min
(c) 46.2 min (d) 22.7 min

9. The two main differences between RNA and DNA are

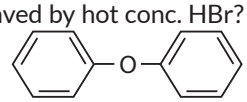
(a) ribose sugar and thymine in RNA
(b) deoxyribose sugar and uracil in DNA
(c) ribose sugar and uracil in RNA
(d) deoxyribose sugar and guanine in DNA.

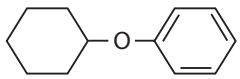
10. The given graph shows the vapour pressure-temperature curves for some liquids.

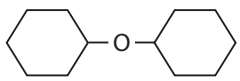


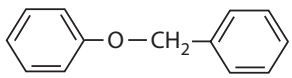
Liquids *A*, *B*, *C* and *D* respectively are
(a) diethyl ether, acetone, ethyl alcohol, water
(b) acetone, ethyl alcohol, diethyl ether, water
(c) water, ethyl alcohol, acetone, diethyl ether
(d) ethyl alcohol, acetone, diethyl ether, water.

11. Which of the following ethers is unlikely to be cleaved by hot conc. HBr?

(a) 

(b) 

(c) 

(d) 

12. Which of the following aldehydes will undergo Cannizzaro reaction?
(a) Ethanal
(b) 2-Methylpropanal
(c) 2,2-Dimethylpropanal
(d) Phenylacetaldehyde

13. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A) : H_2 – O_2 fuel cell is generally used in Apollo space programme.

Reason (R) : The fuel cell uses the reaction of hydrogen with oxygen to provide electrical power and water.

Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

14. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A) : Aniline undergoes electrophilic substitution at *ortho* and *para*-positions.

Reason (R) : Gabriel phthalimide reaction produces only primary amines.

Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

15. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A) : In high spin complex, configuration of d^5 ions will be $t_{2g}^3\, e_g^2$.

Reason (R) : In high spin complex, pairing energy is less than crystal field energy.

Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R).

Assertion (A) : Formaldehyde cannot be prepared by Rosenmund's reduction.

Reason (R) : Acid chlorides can be reduced into aldehydes with hydrogen in boiling xylene using palladium or platinum as a catalyst supported on barium sulphate. This is known as Rosenmund's reduction.

Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION-B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. (a) Write the product obtained when *D*-glucose reacts with $H_2N{-}OH$.
(b) Water soluble vitamins must be supplied in diet regularly. Why?

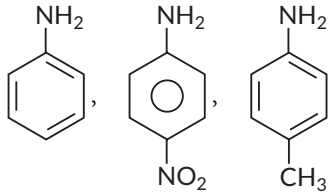
OR

(a) What is the structural difference between a nucleoside and a nucleotide?
(b) "The two strands of DNA are not identical but are complementary." Explain.

18. A bottle of commercial sulphuric acid (density = 1.787 g/mL) is labelled as 86 percent by weight. What is the molarity of the acid?

19. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol
(ii) Ethyl magnesium bromide to propan-1-ol

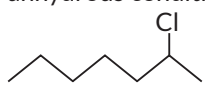
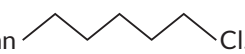
20. (a) Show the steps of reactions in the Stephen's method for production of acetaldehyde.
(b) What is paraformaldehyde?

21. Arrange the following in increasing order of their basic strength :
(i) $C_6H_5—NH_2$, $C_6H_5—CH_2—NH_2$, $C_6H_5—NH—CH_3$
(ii) 

SECTION-C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. (i) The first two ionisation enthalpies of lanthanoids are comparable with those of calcium. Explain.
(ii) Explain :
(a) Why is europium (II) more stable than cerium (II)?
(b) Why is +3 oxidation state of gadolinium (Z = 64) and lutetium (Z = 71) especially stable?

23. Explain the following observations:
(i) Grignard reagents are prepared strictly under anhydrous conditions.
(ii)  undergoes faster S_N1 reaction than 
(iii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

24. Predict towards which electrode would an α-amino acid migrate in an electric field at
(a) pH < pI,
(b) pH > pI
Explain.

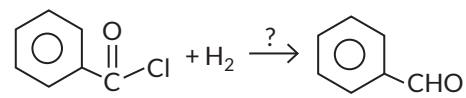
25. (a) In the button cell widely used in watches, the following reaction takes place :
$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$
Determine $E°$ and $\Delta G°$ for the reaction.
(Given: $E°_{Ag^+/Ag}$ = 0.80 V, $E°_{Zn^{2+}/Zn}$ = – 0.76 V)
(b) What will be the pH of the following half-cell ?
Pt, H_2 | H_2SO_4
The oxidation potential is + 0.3005 V.

OR

(a) For the cell $Zn_{(s)}|Zn^{2+}_{(aq)} \,||\, Cu^{2+}_{(aq)}|Cu_{(s)}$, derive the relation between $E°_{cell}$ and K_c at 298 K.
(b) A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential ($E°_{Zn^{2+}/Zn}$ = –0.76 V).

26. Complete the following chemical equations:
(i) $CH_3CH_2Cl \xrightarrow{NaCN} (A) \xrightarrow[Ni/H_2]{Reduction} (B)$
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$
(iii) $R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4}$

27. The density of a 3 M sodium thiosulphate solution is 1.25 g mL^{-1}. Calculate
(i) the % by weight of sodium thiosulphate
(ii) the mole fraction of sodium thiosulphate and
(iii) the molalities of Na^+ and $S_2O_3^{2-}$ ions.

28. Write the reagents required in the following reactions.
(i) $CH_2=CH-CH_2OH \xrightarrow{?} CH_2=CH-CHO$
(ii) $CH_3(CH_2)_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{?}$ $CH_3(CH_2)_3-\overset{\overset{O}{\|}}{C}-H$
(iii) 

SECTION-D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. Electrical work done in unit time is equal to electrical potential multiplied by total charge passed. In order to obtain maximum work from a cell, the charge has to be passed reversibly. The reversible work done by a cell is equal to decrease in its Gibb's energy. Hence, Gibb's energy of reaction is given by

$$\Delta G = -nFE_{cell}$$

Hence, E is the emf of the cell and nF is the amount of energy.

Answer the following questions:

(a) How is equilibrium constant of a reaction is related to standard emf of a cell?

OR

The emf ($E°_{cell}$) of the cell reaction $3Sn^{4+} + 2Cr \rightarrow 3Sn^{2+} + 2Cr^{3+}$ is 0.89 V.

Calculate $\Delta G°$ for the reaction.

(F = 96500 C)

(b) The standard electrode potential ($E°$) for Daniell cell is +1.1 V. Calculate the $\Delta G°$ for the reaction.

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(1 F = 96500 C mol^{-1})

(c) Calculate the cell emf at 25°C for the following cell :

$Mg_{(s)} \mid Mg^{2+}$ (0.01 M) $\parallel Sn^{2+}$ (0.1 M) $\mid Sn_{(s)}$

[Given $E°_{(Mg^{2+}/Mg)} = -2.34$ V ; $E°_{(Sn/Sn^{2+})} = -0.136$ V

1 F = 96500 (mol^{-1})].

Calculate the maximum work that can be accomplished by the operation of this cell.

30. Potassium dichromate acts as a strong oxidising agent in acidic medium. When heated with a metal chloride and conc. sulphuric acid, it gives orange red fumes. On passing these fumes through sodium hydroxide, it gives a yellow solution of Na_2CrO_4 and this acidified yellow solution gives yellow precipitate, $PbCrO_4$ with lead acetate.

Answer the following questions:

(a) What is oxidation state of 'Cr' in potassium dichromate?

(b) Name the main product formed when $K_2Cr_2O_7$ reacts with NaCl in acidic medium.

(c) Draw the structure of dichromate ion.

OR

Potassium dichromate is used as primary standard in volumetric analysis. Explain.

SECTION-E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt **any five** of the following :

(a) Out of 2-chloroethanol and ethanol which is more acidic and why?

(b) Alcohols react with active metals *e.g.*, Na, K etc. to give corresponding alkoxides. Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols.

(c) Anisole on reaction with HI results in the formation of CH_3I and not C_6H_5I. Why?

(d) Boiling points of alcohols are higher than corresponding hydrocarbons, ethers and alkyl halides.Why?

(e) *o*-Nitrophenol is steam volatile while *p*-nitrophenol is not. Why?

(f) What happens when phenol is treated with bromine water?

(g) C–O–C bond angle in ethers (111.7°) is slightly larger than the tetrahedral angle. Why?

32. (a) Explain hybridisation in the complex which contains hexacyanoferrate(III) ion.

(b) Based on the V.B. theory describe the formation and nature of hexaamminecobalt(III) chloride.

OR

(a) Compare the magnetic behaviour of the complex entities $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$. [Atomic number of Fe = 26]

(b) Give the formula of each of the following coordination entities :

(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylenediamine (*en*) molecules.

(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behaviour of each of the above coordination entities.

33. The initial rate of reaction : $A + 5B + 6C \longrightarrow 3D + 3E$ has been determined by measuring the rate of disappearance of A under the following conditions :

Expt. No.	$[A]_0$ (M)	$[B]_0$ (M)	$[C]_0$ (M)	Initial rate (M min^{-1})
1.	0.02	0.02	0.02	2.08×10^{-3}
2.	0.01	0.02	0.02	1.04×10^{-3}
3.	0.02	0.04	0.02	4.16×10^{-3}
4.	0.02	0.02	0.04	8.32×10^{-3}

(i) Determine the order of reaction with respect to each reactant.

(ii) What is the rate constant?

(iii) Calculate the initial rate of the reaction when the concentration of all the reactants is 0.01 M.

OR

(i) Two reactions of the same order have equal pre-exponential factors but their activation energies differ by 24.9 kJ mol^{-1}. Calculate the ratio between the rate constants of these reactions at 27°C. (R = 8.3 J K^{-1} mol^{-1})

(ii) An exothermic reaction, $A \longrightarrow B$ has an activation energy of 17 kJ per mole of A. The heat of the reaction is 40 kJ. Calculate the activation energy for the reverse reaction $B \longrightarrow A$.

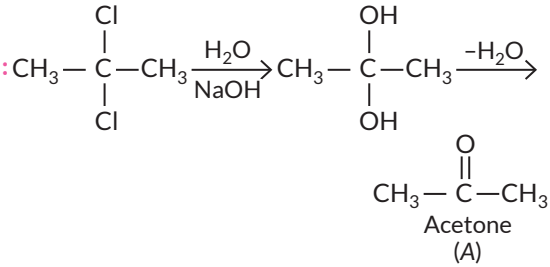
Detailed SOLUTIONS

1. (a): $[R] = [R]_0 - kt$

For completion of reaction, $[R] = 0$

or $t = \dfrac{[R]_0}{k}$

2. (c):



3. (c): $\pi = CRT$, $y = mx$ type graph so, slope is given by RT.

4. (c)

5. (c): It is a reducing sugar. The free aldehyde group can be produced at C-1 of second glucose in solution and it shows reducing properties.

6. (c): The reaction that occurs will be

$Pb^{2+} + Fe \longrightarrow Fe^{2+} + Pb$

On adding Fe and Pb, Fe will be consumed to increase the concentration of Fe^{2+}.

7. (b): The reaction between an alkyl halide and an aryl halide in presence of sodium and dry ether is known as Wurtz-Fittig reaction.

8. (a): 30% decomposition means X = 30% of R_0

or $R = R_0 - 0.3R_0 = 0.7R_0$

For first order, $k = \dfrac{2.303}{t}\log\dfrac{[R_0]}{[R]}$

$$= \frac{2.303}{40}\log\frac{10}{7}\text{min}^{-1} = 8.918\times10^{-3}\,\text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918\times10^{-3}\,\text{min}^{-1}} = 77.7\ \text{min}$$

9. (c): RNA contains ribose sugar and uracil while DNA contains deoxyribose sugar and thymine.

10. (a): The vapour pressure increases with decrease in intermolecular forces. When the forces are weak, the liquid has high volatility and maximum vapour pressure. Diethyl ether has highest vapour pressure while water has lowest vapour pressure.

11. (a): Diphenyl ethers are not cleaved by hot conc. HBr or HI.

12. (c): 2,2-Dimethylpropanal does not have α-H atom, and hence undergoes Cannizzaro reaction.

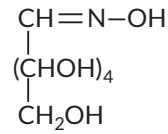
13. (a): Except electrical power, the water vapours produced during the reaction are condensed and added to the drinking water supply for the astronauts. So, H_2–O_2 fuel cell is used in Apollo space programme.

14. (b)

15. (c): In high spin complex, $\Delta_o < P$ and in d^5 configuration, 4th and 5th electron are added to e_g rather than t_{2g}. So, configuration of d^5 ion will be $t_{2g}^3\, e_g^2$.

16. (b): HCHO cannot be prepared by Rosenmund's reduction because formyl chloride is unstable at room temperature.

17. (a) *D*-glucose reacts with $H_2N{-}OH$ to give glucose oxime.

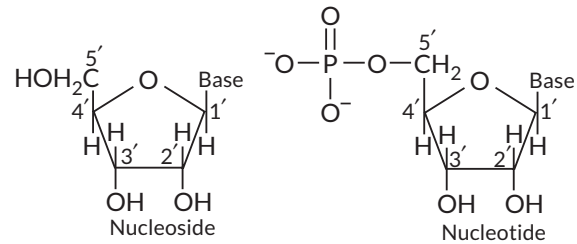


(b) Since water soluble vitamins are soluble in water and excreted in urine so, they must be supplied regularly.

OR

(a) A unit formed by attachment of a base to C-1′ position of sugar is known as nucleoside.

When nucleoside is linked to phosphate group at C-5′ position of sugar moiety, resulting species is called nucleotide.



Nucleosides contain only two components, a pentose sugar and a nitrogenous base.

Nucleotides contain all the three components, a pentose sugar, a nitrogenous base and a phosphate group.

(b) James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are bonded to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine (A═T) whereas cytosine forms hydrogen bonds with guanine (C≡G).

Due to this base pairing principle, the sequence of bases in one strand automatically fixes the sequence of bases in the other strand. Thus, the two strands are complementary and not identical.

18. 86% H_2SO_4 means 100 g of the solution contains 86 g of sulphuric acid.

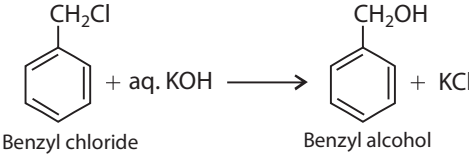
Volume of the 100 g of acid

$$= \frac{\text{Mass}}{\text{Density}} = \frac{100\,\text{g}}{1.787\,\text{g/mL}} = 55.9\ \text{mL}$$

Moles of solute $= \dfrac{86}{98}$

$$\text{Molarity} = \frac{\text{Moles of solute}\times1000}{\text{Vol. of solution (mL)}} = \frac{86}{98}\times\frac{1000}{55.9} = 15.7\,\text{M}$$

19. (i)



(ii) $HCHO + CH_3CH_2MgBr \longrightarrow CH_3CH_2-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-OMgBr$

Formaldehyde; Ethyl magnesium bromide

$\xrightarrow{H_2O} CH_3CH_2CH_2OH + Mg(OH)Br$

Propan-1-ol

20. (a) Stephen's method:

An alkyl cyanide is dissolved in ether, or better, in ethyl formate or ethyl acetate, and reduced with stannous chloride and hydrochloric acid, and then steam distilled.

$R-CN + SnCl_2 + HCl \longrightarrow RCH=NH \xrightarrow{H_3O^+} RCHO$

(b) When an aqueous solution of formaldehyde is evaporated to dryness, a white crystalline solid with fishy odour is obtained which is known as paraformaldehyde.

$nHCHO \xrightarrow{\Delta} (HCHO)_n$

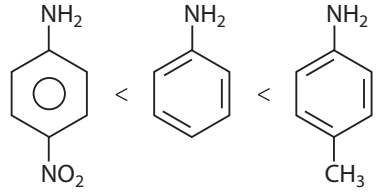
paraformaldehyde

n = 6 to 50

On rapid heating, it gives black gaseous formaldehyde.

21. Increasing order of basic strength :

(i) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(ii) 

22. (i) Last electronic configuration of lanthanoids is similar to that of calcium.

Ln – [Xe]$4f^{1-14}\,5d^{0-1}\,6s^2$

Therefore, first two ionisation enthalpies of lanthanoids are comparable with Ca.

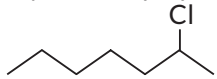
(ii) (a) Europium(II) has electronic configuration [Xe]$4f^7 5d^0$ while cerium (II) has electronic configuration [Xe]$4f^1 5d^1$. In Eu^{2+}, 4*f* subshell is half filled and 5*d*-subshell is empty. Since half filled and completely filled electronic configurations are more stable, hence Eu^{2+} ions is more stable than Ce^{2+}.

(b) This is because gadolinium in +3 state has half filled 4*f*-subshell ($4f^7$) and lutetium in +3 state has completely filled 4*f*-subshell which are very stable configurations.

23. (i) Grignard reagents react with water to form alkanes.

$R-Mg-X + H_2O \longrightarrow R-H + Mg\begin{matrix}X\\OH\end{matrix}$

So, they must be prepared under anhydrous conditions.

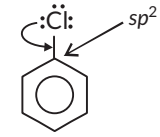
(ii) 

undergoes faster S_N1 reaction as it is a secondary halide and gives more stable carbocation than primary halide.

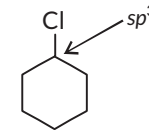
(iii) There are two reasons :

(a) In case of chlorobenzene, carbon to which chlorine is attached is sp^2-hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3-hybridised. So, the net dipole moment is lower in chlorobenzene.

(b) In chlorobenzene, C – Cl bond has some double bond character so its bond length is smaller. Hence, dipole moment is smaller than cyclohexyl chloride which has a longer C – Cl single bond.



Chlorobenzene



Cyclohexyl chloride

24. Isoelectric point of an amino acid is that pH at which there is no net migration of the amino acid occurs in an electric field. It is sometimes represented as pI.

Therefore,

(a) Below the pI (pH < pI), the zwitter ion will accept H^+ and exist as the cation.

$\overset{+}{N}H_3-\underset{R}{\underset{|}{CH}}-COO^- + H^+ \longrightarrow H_3\overset{+}{N}-\underset{R}{\underset{|}{CH}}-COOH$

Therefore, migration will be towards the cathode.

(b) Above the pI (pH > pI), the zwitter ion will release proton and will exist as anion.

$\overset{+}{N}H_3-\underset{R}{\underset{|}{CH}}-COO^- \longrightarrow H_2N-\underset{R}{\underset{|}{CH}}-COO^-$

Therefore, migration will be towards the anode.

25. (a) $E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Zn^{2+}/Zn}$

$= 0.80 - (-0.76) = 1.56$ V

$\Delta G^\circ_{cell} = -nFE^\circ_{cell} = -2 \times 96500 \times 1.56$

$= -301.08$ kJ mol^{-1}

(b) Reduction reaction at Pt electrode :

$H^+ + e^- \longrightarrow 1/2H_2$

Applying Nernst equation,

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.0591}{1}\log\frac{1}{[H^+]}$$

$$-0.3005 = 0 - \frac{0.0591}{1}\text{pH} \qquad [\text{pH} = -\log[H^+]]$$

$$\text{pH} = \frac{0.3005}{0.0591} = 5.085$$

OR

(a) In this cell, electrons will flow from Zn electrode to Cu electrode.

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$

Apply the law of mass action,

$$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (\because [Cu_{(s)}] = [Zn_{(s)}] = 1)$$

According to Nernst equation for cell potential,

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium E_{cell} is zero.

$$\therefore \quad E^\circ_{cell} = \frac{2.303RT}{nF}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{2.303RT}{nF}\log K_c$$

or $\log K_c = \frac{n \times 96500}{2.303 \times 8.314 \times 298} E^\circ_{cell}$

$\log K_c = \frac{n}{0.059} E^\circ_{cell}$

$E^\circ_{cell} = \frac{0.059}{n} \log K_c = \frac{0.059}{2} \log K_c$ [$\because n = 2$ for Zn^{2+} and Cu^{2+} cell]

(b) The electrode reaction written as reduction reaction is $Zn^{2+} + 2e^- \rightarrow Zn$ ($n = 2$)

Applying Nernst equation, we get

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

$[Zn^{2+}] = \frac{95}{100} \times 0.1\ M = 0.095\ M$

$\therefore \quad E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095}$

$= -0.76 - 0.02955\ (\log 1000 - \log 95)$

$= -0.76 - 0.02955\ (3 - 1.9777)$

$= -0.76 - 0.03021 = -0.79021\ V$

26. (i) $CH_3CH_2Cl \xrightarrow[(A)]{NaCN} CH_3CH_2CN \xrightarrow[Ni/H_2]{Reduction} \underset{(B)}{CH_3CH_2CH_2NH_2}$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$

(iii) $R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$

27. (i) Calculation of % by weight of $Na_2S_2O_3$:

Density of 3 M $Na_2S_2O_3$ solution = 1.25 g/mL

Weight of 1000 mL of $Na_2S_2O_3$ solution = 1.25×1000 = 1250 g

Since, 1 mole of $Na_2S_2O_3 = (23 \times 2) + (32 \times 2) + (16 \times 3) = 158$

Weight of $Na_2S_2O_3$ in 1000 mL of 3 M solution = 3×158 = 474 g

1250 g of solution contain = 474 g $Na_2S_2O_3$

100 g of solution contain = $\frac{474 \times 100}{1250}$ = 37.92 g $Na_2S_2O_3$.

$\therefore$ % by weight of sodium thiosulphate = 37.92%.

(ii) Calculation of mole fraction of $Na_2S_2O_3$:

100 g of the solution contains = 37.92 g $Na_2S_2O_3$ and (100 – 37.92) g = 62.08 g water.

Number of moles of $Na_2S_2O_3$ in 37.92 g of $Na_2S_2O_3$ = $\frac{37.92}{158}$ = 0.24 moles

Similarly, number of moles of H_2O in 62.08 g of water = $\frac{62.08}{18}$ = 3.45 moles

$\therefore$ Total number of moles = 0.24 + 3.45 = 3.69 moles.

$\therefore$ Mole fraction of $Na_2S_2O_3 = \frac{0.24}{3.69}$ = 0.065 moles.

(iii) Calculation of molalities of Na^+ and $S_2O_3^{2-}$ ions :

62.08 g of water contain = 0.24 moles of $Na_2S_2O_3$

1000 g of water contain = $\frac{0.24 \times 1000}{62.08}$ moles

= 3.865 moles of $Na_2S_2O_3$

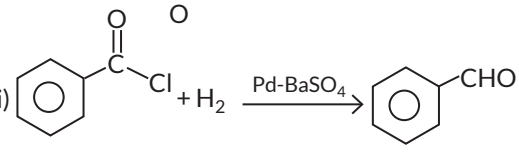
Since 1 mole of $Na_2S_2O_3$ contains 2 moles of Na^+ and 1 mole of $S_2O_3^{2-}$ ions,

$\therefore$ Molality of $Na^+ = 2 \times 3.865 = 7.730$ m

Similarly, molality of $S_2O_3^{2-} = 1 \times 3.865 = 3.865$ m

28. (i) $CH_2{=}CH{-}CH_2OH \xrightarrow{PCC} CH_2{=}CH{-}CHO$

(ii) $CH_3(CH_2)_3{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5 \xrightarrow[H_2O]{DIBAL-H} CH_3(CH_2)_3{-}\overset{\overset{O}{\|}}{C}{-}H$

(iii) 

29. (a) $\Delta G^\circ = -nFE^\circ_{cell}$

$-RT \ln K = -nFE^\circ_{cell}$

$E^\circ_{cell} = \frac{RT \ln K}{nF}$ or $E^\circ_{cell} = \frac{2.303RT}{nF} \log_{10} K$

OR

The given cell reaction is

$3Sn^{4+}_{(aq)} + 6e^- \rightarrow 3Sn^{2+}_{(aq)}$

$2Cr_{(s)} \rightarrow 2Cr^{3+} + 6e^-$

$3Sn^{4+} + 2Cr \rightarrow 3Sn^{2+} + 2Cr^{3+}$

Number of electrons transferred = 6, $E^\circ = 0.89$ V

$\Delta_r G^\circ = -nFE^\circ$

$= -6 \times 96500\ C \times 0.89\ V = -515310\ J = -515.31\ kJ$

(b) Here, $n = 2$, $E^\circ_{cell} = 1.1$ V, $F = 96487\ C\ mol^{-1}$

$\Delta_r G^\circ = -nFE^\circ_{cell}$

$\Delta_r G^\circ = -2 \times 1.1 \times 96487$

$= -212271.4\ J\ mol^{-1} = -212.2714\ kJ\ mol^{-1}$

(c) $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$ (Anode half reaction)

$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ (Cathode half reaction)

$Mg_{(s)} + Sn^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Sn_{(s)}$ (Net cell reaction)

$E^\circ_{cell} = E^\circ_{Sn^{2+}/Sn} - E^\circ_{Mg^{2+}/Mg} = -0.136 + 2.34 = 2.204$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{0.01\ M}{0.10\ M}$$

$= 2.20 - (0.0295 \times -1) = 2.2295$

$W_{max} = -\Delta G^\circ = -(-nFE^\circ_{cell}) = nFE^\circ_{cell}$

$= 2 \times 96500 \times 2.204 = 425372\ J = 425.372\ kJ$

30. (a) $K_2Cr_2O_7 \Rightarrow 2 + 2x + 7(-2) = 0$

$2 + 2x - 14 = 0$

$2x = +12$

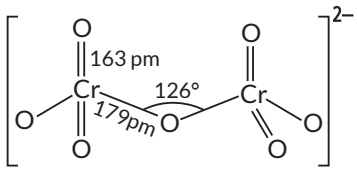
$x = +6$

Therefore, oxidation state of Cr in $K_2Cr_2O_7$ is +6.

(b) Chromyl chloride, CrO_2Cl_2

$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 2KHSO_4 + 3H_2O + 4NaHSO_4$

(c)



OR

Potassium dichromate ($K_2Cr_2O_7$) is used as primary standard in volumetric analysis because it is available in very pure state, it is non-hygroscopic and it does not decolourise in solution. Hence its standard solution can be prepared by dissolving known amount in known volume.

31. (a) Out of CH_3CH_2OH and $ClH_2C\text{-}CH_2OH$, 2-Chloroethanol is more acidic due to $-I$ effect of chlorine atom, –Cl group withdraws electrons from the carbon chain making O–H bond weaker and more acidic.

(b) The order of reactivity of alcohols with sodium metal is of the order : Primary > Secondary > Tertiary.

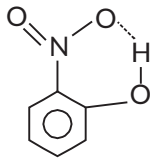
Electron releasing inductive effect of alkyl group in alcohols increases the electron density around O–H bond which makes the O–H bond stronger and makes the alcohol a weaker acid. More the number of alkyl groups, stronger is the O–H bond and weaker is the acidity of alcohol.

(c) In case of anisole, methyl phenol oxonium ion is formed $C_6H_5-\overset{+}{\underset{|}{O}}(H)-CH_3$.

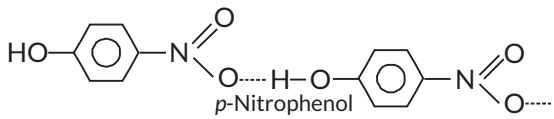
The bond O – CH_3 is weaker than O – C_6H_5 because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore the attack of I^- ion breaks O – CH_3 bond, and CH_3I is formed instead of C_6H_5I.

(d) The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers, hydrocarbons and alkyl halides.

(e) *o*-Nitrophenol is steam volatile due to intramolecular H–bonding. *p*-Nitrophenol is not steam volatile due to presence of intermolecular H–bonding.

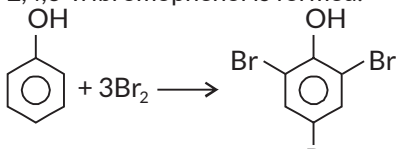


o-Nitrophenol



p-Nitrophenol

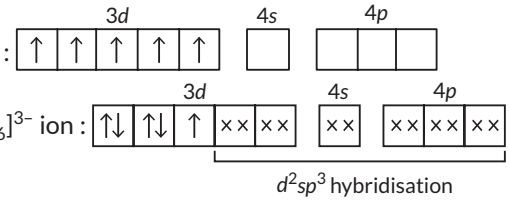
(f) 2,4,6-Tribromophenol is formed.



2, 4, 6-Tribromophenol

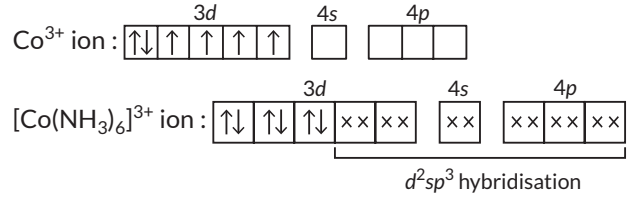
(g) Due to repulsive interaction between two bulkier alkyl (–*R*) groups.

32. (a) Formation of hexacyanoferrate(III) ion; $[Fe(CN)_6]^{3-}$: Electronic configuration of iron in the ground state is $3d^64s^2$. The oxidation state of iron is +3 in this complex. Iron (III) has outer electronic configuration $3d^54s^0$. It has been experimentally observed that this complex has one unpaired electron. To account for this, two unpaired electrons in 3*d* subshell pair up, thus leaving two 3*d*-orbitals empty. These two vacant 3*d*-orbitals, alongwith one 4*s*-orbital and three 4*p*-orbitals hybridise to give six equivalent d^2sp^3 hybridised orbitals. Six pairs of electrons, one from each cyanide ion, occupy the six vacant hybrid orbitals so produced. The complex has octahedral geometry and is paramagnetic due to the presence of one unpaired electron.



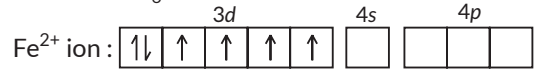
The complex evidently involves $(n-1)d^2ns\ np^3$ hybridisation and is, therefore, called inner orbital or low spin complex.

(b) The outer electronic configuration of cobalt (III) ion is $3d^6$. According to Hund's rule, four of the 3*d*-orbitals are singly filled and one 3*d*-orbital has a pair of electrons. Octahedral complexes are formed through d^2sp^3 hybridisation for which the metal atom must have two of its 3*d*-orbitals empty. This is achieved by the pairing of the two 3*d*-electrons as a result of the energy released due to the approach of the ligands. This results in the formation of an octahedral complex. As it is evident from the figure, the complex does not contain any unpaired electron and is, therefore, diamagnetic.

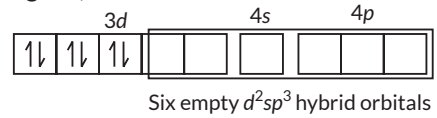


OR

(a) $[Fe(CN)_6]^{4-}$ ion :



Fe^{2+} ion hybridised (under the influence of strong field ligand).



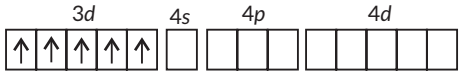
Six empty d^2sp^3 hybrid orbitals

$[Fe(CN)_6]^{4-}$ ion formation :

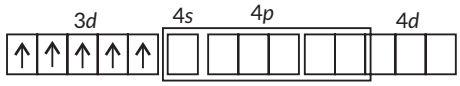
Six pairs of electrons from six CN^- ions (d^2sp^3)

Since, the complex ion does not contain any unpaired electron, so it is diamagnetic.

$[FeF_6]^{3-}$ ion :

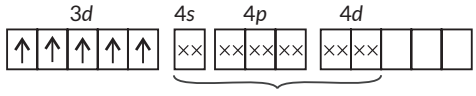
Fe^{3+} ion : 

Fe^{3+} ion hybridised (under the influence of weak field ligand).



Six empty sp^3d^2 hybrid orbitals

$[FeF_6]^{3-}$ ion formation :



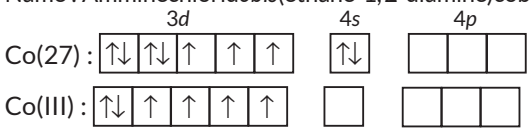
Six electrons pairs from six F^- ions (sp^3d^2)

As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

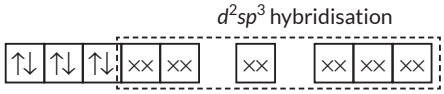
$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9$ B.M.

(b) (i) $[Co(NH_3)(Cl)(en)_2]^{2+}$

Name : Amminechlorido*bis*(ethane-1,2-diamine)cobalt(III) ion



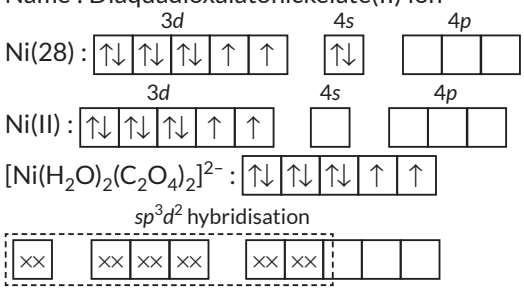
$[Co(NH_3)(Cl)(en)_2]^{2+}$:



Since, there are no unpaired electrons, complex is diamagnetic.

(ii) $[Ni(H_2O)_2(C_2O_4)_2]^{2-}$

Name : Diaquadioxalatonickelate(II) ion



The complex has two unpaired electrons and therefore, it will be paramagnetic.

33. (i) Rate law may be written as :

Rate = $k[A]^a[B]^b[C]^c$

Comparing experiments 1 and 2,

$(Rate)_1 = k(0.02)^a(0.02)^b(0.02)^c = 2.08 \times 10^{-3}$ ...(i)

$(Rate)_2 = k(0.01)^a(0.02)^b(0.02)^c = 1.04 \times 10^{-3}$ ...(ii)

Dividing eq. (i) by eq. (ii) we get,

$$\frac{(Rate)_1}{(Rate)_2} = \frac{(0.02)^a}{(0.01)^a} = \frac{2.08\times10^{-3}}{1.04\times10^{-3}} = 2$$

or $2^a = 2 \quad \therefore \quad a = 1$

Comparing experiments 1 and 3,

$(Rate)_1 = k(0.02)^a(0.02)^b(0.02)^c = 2.08 \times 10^{-3}$ ...(iii)

$(Rate)_3 = k(0.02)^a(0.04)^b(0.02)^c = 4.16 \times 10^{-3}$ ...(iv)

Dividing eq. (iv) by eq. (iii) we get,

$$\frac{(Rate)_3}{(Rate)_1} = \frac{(0.04)^b}{(0.02)^b} = \frac{4.16\times10^{-3}}{2.08\times10^{-3}} = 2$$

$2^b = 2 \quad \therefore \quad b = 1$

Comparing experiments 1 and 4,

$(Rate)_1 = k(0.02)^a(0.02)^b(0.02)^c = 2.08 \times 10^{-3}$ ...(v)

$(Rate)_4 = k(0.02)^a(0.02)^b(0.04)^c = 8.32 \times 10^{-3}$ ...(vi)

Dividing eq. (vi) by eq. (v), we get

$$\frac{(Rate)_4}{(Rate)_1} = \frac{(0.04)^c}{(0.02)^c} = \frac{8.32\times10^{-3}}{2.08\times10^{-3}} = 4$$

or $2^c = 2^2$

$\therefore \quad c = 2$

Therefore, the order of the reaction with respect to *A*, *B* and *C* are 1, 1 and 2 respectively.

Rate = $k[A][B][C]^2$

(ii) Substituting the values from experiment 1, we get

$2.08 \times 10^{-3} = k \times 0.02 \times 0.02 \times (0.02)^2$

$$\therefore \quad k = \frac{2.08\times10^{-3}}{(0.02)^4} = \frac{2.08\times10^{-3}}{16\times10^{-8}} = 1.3 \times 10^4 \text{ M}^{-3} \text{ min}^{-1}$$

(iii) Rate of reaction when concentration of all reactants = 0.01 M

Rate = $1.3 \times 10^4 \times (0.01) \times (0.01) \times (0.01)^2$

$= 1.3 \times 10^{-4}$ M min^{-1}

OR

(i) The Arrhenius equation is : $k = Ae^{-E_a/RT}$

Taking log on both sides, $\log k = \log A - \frac{E_a}{2.303RT}$

For reaction (i), $\log k_1 = \log A - \frac{E_{a(1)}}{2.303RT}$ ...(i)

For reaction (ii), $\log k_2 = \log A - \frac{E_{a(2)}}{2.303RT}$ ...(ii)

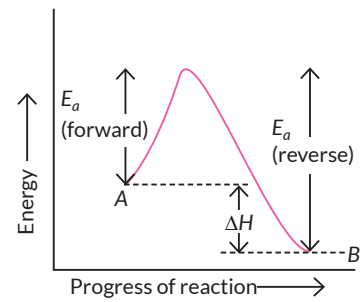
Subtracting (i) from (ii) $\log\frac{k_2}{k_1} = \frac{E_{a(1)} - E_{a(2)}}{2.303RT}$

$$= \frac{24.9\times1000}{2.303\times8.3\times300} = 4.342 \qquad \therefore \quad \frac{k_2}{k_1} = 2.198\times10^4$$

(ii) For the reaction $A \longrightarrow B$.

Activation energy, E_a = 17 kJ.

Since, the reaction is exothermic, the energy of the products is less than that of reactants. The potential energy diagram for such a reaction is given in figure.



From the figure, it is clear that the activation energy for the reverse reaction, $B \longrightarrow A$ is :

E_a (reverse) = E_a (forward) + ΔH = 17 + 40 = 57 kJ.

PRACTICE PAPER 5

General Instructions :

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case-based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION-A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Which of the following has the most acidic hydrogen?
(a) 3-Hexanone (b) 2,4-Hexanedione
(c) 2,5-Hexanedione (d) 2,3-Hexanedione

2. The correct order of increasing oxidising power in the series is
(a) $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$
(b) $Cr_2O_7^{2-} < VO_2^+ < MnO_4^-$
(c) $Cr_2O_7^{2-} < MnO_4^- < VO_2^+$
(d) $MnO_4^- < Cr_2O_7^{2-} < VO_2^+$

3. Which of the following azeotropes is not correctly matched?
(a) HNO_3 (68%) + H_2O (32%) : Maximum boiling azeotrope, boiling point = 393.5 K
(b) H_2O (43%) + HI (57%) : Minimum boiling azeotrope, boiling point = 290 K
(c) C_2H_5OH (95.5%) + H_2O (4.5%) : Minimum boiling azeotrope, boiling point = 351.15 K
(d) Chloroform (93.2%) + C_2H_5OH (6.8%) : Minimum boiling azeotrope, boiling point = 332.3 K

4. The hybridisation involved in complex $[Ni(CN)_4]^{2-}$ is (At. No. of Ni = 28)
(a) sp^3 (b) d^2sp^2
(c) d^2sp^3 (d) dsp^2

5. Reduction of carbonyl group into hydrocarbons using Zn-amalgam and conc.HCl is known as
(a) Dow reduction
(b) Rosenmund reduction
(c) Wolff-Kishner reduction
(d) Clemmensen reduction.

6. Out of the following, the strongest base in aqueous solution is
(a) methylamine (b) dimethylamine
(c) trimethylamine (d) aniline.

7. Vapour pressure of dilute aqueous solution of glucose is 750 mm of mercury at 373 K. The mole fraction of solute is
(a) 1/76 (b) 1/7.6 (c) 1/38 (d) 1/10

8. Which of the following are water soluble vitamins?
1. Vitamin B 2. Vitamin C
3. Vitamin E 4. Vitamin D
(a) 1 and 3 (b) 1 and 2
(c) 3 and 4 (d) 1 and 4

9. The equilibrium constant for the disproportionation reaction :

$2Cu^+_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$ at 25°C is

(Given: $E^\circ_{Cu^+/Cu} = 0.52V$; $E^\circ_{Cu^{2+}/Cu^+} = 0.16\,V$)

(a) 1.2×10^{-6} (b) 6×10^4
(c) 6×10^6 (d) 1.2×10^6

10. The peptide linkage formed between glycine (NH_2CH_2COOH) and alanine ($NH_2CH(CH_3)COOH$) to give glycylalanine can be shown as
(a) $NH_2-CH_2-NH-CH(CH_3)-COOH$
(b) $NH_2-CH_2-CONH-CH(CH_3)-COOH$
(c) $H_2NCOCH_2-CH(CH_3)-CONH_2$
(d) $HOOC-CH_2-NH-NH-CH(CH_3)-COOH$

11. The reduction of which of the following compounds would yield secondary amine?
(a) Primary amine
(b) Carbylamine
(c) Alkyl nitrile
(d) Secondary nitro compound

12. Aldol condensation product of acetone on dehydration gives
(a) but-2-enal
(b) 2-methylpent-3-en-4-one
(c) 4-hydroxy-4-methylpentan-2-one
(d) 4-methylpent-3-en-2-one.

13. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Co(IV) is known but Ni(IV) is not.
Reason (R) : Ni(II) has d^8 electronic configuration.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

14. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Rate of hydrolysis of methyl chloride to methanol is higher in DMF than in water.
Reason (R) : Hydrolysis of methyl chloride follows second order kinetics.
Select the most appropriate answer from the options given below :
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

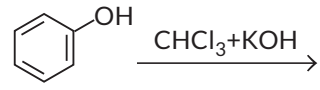
15. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : $KMnO_4$ acts as an oxidising agent in acidic, basic or neutral medium.
Reason (R) : It oxidises ferrous sulphate to ferric sulphate.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Boiling points of alcohols are lower than hydrocarbons.
Reason (R) : Among isomeric alcohols, boiling point decreases in the order : 1° > 2° > 3°.
Select the most appropriate answer from the options given below :
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

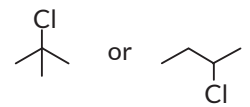
SECTION-B

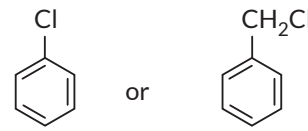
This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. (a) Why is phenol is acidic and hexanol is neutral towards a solution of NaOH?
(b) Predict the product of the following reaction:



18. Aqueous copper sulphate solution (blue in colour) gives a green precipitate with aqueous potassium fluoride and a bright green solution with aqueous potassium chloride.

19. (i) Identify the compound which will undergo SN1 reaction.
(a) 

(b) 

(ii) Arrange the following halides in order of increasing S_N2 reactivity.
CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$

20. Complete the following reactions :
(i) $CH_3CHO \xrightarrow{NaOH}$
(ii) $(A) \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3CH_2CH_3$

21. A solution of *A* and *B* with 30 mole percent of *A* is in equilibrium with its vapour which contain 60 mole per cent of *A*. Assuming that the solution and the vapour behave ideally, calculate the ratio of the vapour pressures of pure *A* and pure *B*.

OR

Non-ideal solution exhibit either positive or negative from Raoult's law. What are these deviation and why are they caused? Explain with one example for each type.

SECTION-C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. (a) Write the complete reaction for each of the following conversions stating the conditions necessary :
(i) Toluene to benzaldehyde
(ii) Aldehyde to acetal.
(b) Describe the preparation of acetic acid from acetylene.

23. (a) What type of a battery is lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery.
(b) Corrosion is an electrochemical phenomenon. Explain.

24. (a) Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly.
(b) Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment?
(c) Explain the given trend in the boiling point of the following :
MeI > MeBr > MeCl > MeF > CH_4

25. Explain :
(i) What will be the correct order for the wavelength of absorption in the visible region for the following :
$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?
(ii) $[Ni(H_2O)_6]^{2+}$ is green and becomes violet when ethane-1, 2-diamine is added to it.

26. When *tert*-butanol and *n*-butanol are separately treated with a few drops of dil. $KMnO_4$, in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

OR

An organic liquid (*A*), containing C, H and O with boiling point 78°C and possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product (*B*) with the empirical formula, CH_2. *B* decolourises bromine water as well as alkaline $KMnO_4$ solution and takes up one mole of H_2 (per mole of *B*) in the presence of finely divided nickel at high temperature. Identify the substances *A* and *B*.

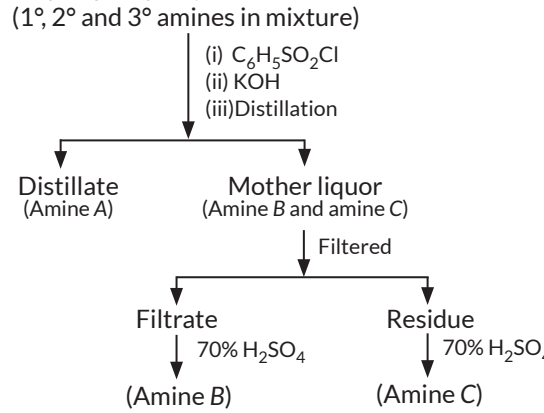
27. (i) Calculate van't Hoff factor for dilute solution of glucose.
(ii) A solution of 7.45 g KCl in 1000 mL shows osmotic pressure 4.68 atm at 300 K. Calculate degree of dissociation.

28. Half life period of first order reaction at 47°C is 10 min and at 27°C is 30 min. Calculate the activation energy of the reaction.

SECTION-D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. When the mixture contains the three amine salts (1°, 2° and 3°) along with quaternary salt, it is distilled with KOH solution. The three amines distill, leaving the quaternary salt unchanged in the solution. Then the mixture of amines is separated by fractional distillation, Hinsberg's method and Hoffmann's method.



Answer the following questions:
(a) What is Hinsberg's reagent?
(b) What does primary amine with Hinsberg's reagent form?
(c) What does secondary amine with Hinsberg's reagent form?

OR

What does 3° amine with Hinsberg's reagent give?

30. According to collision theory, products are formed only when the reactant molecules come close and collide together at one and the same time. During the collision, atomic rearrangement takes place which leads to the formation of products. Atomic rearrangement involves breaking and formation of bonds. Atomic rearrangement can take place only when the colliding molecules have energy equal to or greater than the minimum energy required for the rearrangement. If molecule do not possess, this much amount of minimum energy atomic rearrangement will not take place and no product will be formed. The difference between the minimum energy required to bring about atomic rearrangement and the average energy of reactant is called 'energy of activation' (E_a) *i.e.*, energy of reactant molecule in addition to that energy which it possesses already, to bring about a chemical change is called activation energy.

Answer the following questions :

(a) Define activation energy of a reaction.

OR

What is the effect of adding a catalyst on

(i) Activation energy (E_a), and

(ii) Gibbs energy (ΔG) of a reaction?

(b) State the role of activated complex in a reaction and state its relation with activation energy.

(c) The rate constant for the first order decomposition of H_2O_2 is given by the following equation :

$$\log k = 14.2 - \frac{1.0\times10^4}{T}K$$

Calculate E_a for this reaction and rate constant k if its half-life period is 200 minutes.
(Given : R = 8.314 J $K^{-1}mol^{-1}$)

SECTION-E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt **any five** from the following:

(a) How do components of starch differ from each other structurally?

(b) Give an example of acidic amino acid. Why it is acidic?

(c) Give chemical name of vitamin B2? Name the disease caused due to its deficiency.

(d) If one strand of DNA has the sequence ATCGTCCA. What will be the sequence of complementary strand?

(e) What are the hydrolysis products of DNA?

(f) What is the effect of denaturation on the structure of protein?

(g) Fructose contains a keto group but still reduces Tollens' reagent why?

32. (a) Calculate standard emf of the cell in which following reaction takes place at 25°C.

$Cu_{(s)} + Cl_{2(g)} \rightleftharpoons Cu^{2+} + 2Cl^-$

$E°_{Cl_2/Cl^-}$ = +1.36 V, $E°_{Cu^{2+}/Cu}$ = + 0.34 V

Also calculate standard free energy change and equilibrium constant of the reaction.

(b) The emf of a galvanic cell composed of two hydrogen electrodes is 0.16 volt at 25°C. Calculate pH of the anode solution if the cathode is in a solution with pH = 1.

OR

(a) Calculate the cell emf and ΔG for the cell reaction at 25°C for the cell :

$Zn_{(s)} \mid Zn^{2+}$ (0.0004 M) || Cd^{2+} (0.2 M) $\mid Cd_{(s)}$

$E°$ values at 25°C : Zn^{2+}/Zn = – 0.763 V;

Cd^{2+}/Cd = – 0.403 V; F = 96500 C mol^{-1};

R = 8.314 J K^{-1} mol^{-1}.

(b) If $E°$ for copper electrode is 0.34 V, how will you calculate its emf value when the solution in contact with it is 0.1 M in copper ions? How does emf for copper electrode change when concentration of Cu^{2+} ions in the solution is decreased?

33. (a) (i) Out of the ions Ag^+, Co^{2+} and Ti^{4+} which will be coloured in aqueous solution?

(ii) If each one of the above ionic species is placed in a magnetic field, how will they respond and why?

(b) Explain the following :

(i) Acidified $K_2Cr_2O_7$ solution turns green when sodium sulphite is added.

(ii) A ferrous salt decolourises acidified $KMnO_4$ solution.

OR

(a) Write the steps involved in the preparation of

(i) $K_2Cr_2O_7$ from Na_2CrO_4

(ii) $KMnO_4$ from K_2MnO_4

(b) What is meant by lanthanoid contraction? What effect does it have on the chemistry of the elements which follow lanthanoid contraction?

Detailed SOLUTIONS

1. **(b):** $H_3C-\underset{\underset{O}{\|}}{C}-\overset{*}{C}H_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

2,4-Hexanedione

The most acidic hydrogen is the hydrogen attached to $\overset{*}{C}$ as its conjugate base is highly stabilised due to extensive delocalisation of lone pair of electrons as compared to all others.

2. **(a):** Greater the oxidation state of the central metal ion, higher is the oxidising power.

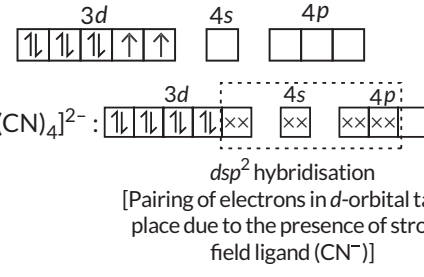
∴ Order of oxidising power is

$\overset{+5}{VO_2^+} < \overset{+6}{Cr_2O_7^{2-}} < \overset{+7}{MnO_4^-}$

3. **(b):** H_2O(43%) and HI(57%) make maximum boiling azeotropic mixture on boiling at 400K.

4. **(d):** $[Ni(CN)_4]^{2-}$: Oxidation number of Ni = +2

Electronic configuration of Ni^{2+} : $3d^8 4s^0$



dsp^2 hybridisation

[Pairing of electrons in d-orbital takes place due to the presence of strong field ligand (CN^-)]

5. **(d):** This is known as Clemmensen reduction.

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Conc.HCl}]{\text{4[H] Zn-Hg}} CH_3-CH_2-CH_3 + H_2O$$

6. (b): The order of basicity of the given compounds is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$.
There is a subtle interplay of the inductive effect, solvation effect and steric hindrance of alkyl groups which decides the basic strength of alkyl amines in the aqueous state.

7. (a): $p_s = p_1°(1 - x_2)$

$\Rightarrow \quad 750 = 760(1 - x_2) \quad$ or, $\dfrac{750}{760} = 1 - x_2$

or, $\dfrac{750}{760} - 1 = -x_2 \quad \Rightarrow \quad x_2 = \dfrac{1}{76}$

8. (b)

9. (d): $2Cu^+_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$

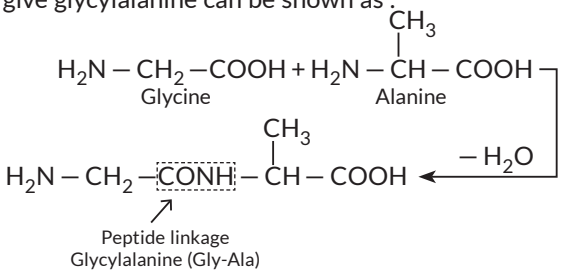
$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{1}\log\frac{[Cu^{2+}_{(aq)}]}{[Cu^+_{(aq)}]^2} \qquad [n = 1]$$

where, $\dfrac{[Cu^{2+}_{(aq)}]}{[Cu^+_{(aq)}]^2} = K_c$, $E_{cell} = 0$

Hence, $\log K_c = \dfrac{E^\circ_{cell}}{0.0591} = \dfrac{0.52 - 0.16}{0.0591} = 6.09$

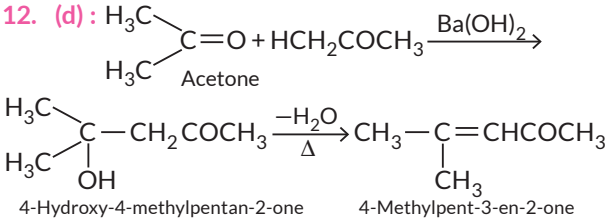
$K_c = 1.2 \times 10^6$

10. (b): The peptide linkage formed between glycine ($H_2N - CH_2 - COOH$) and alanine ($H_2NCH(CH_3) - COOH$) to give glycylalanine can be shown as :



11. (b) : $R - N \equiv C + 2H_2 \xrightarrow{Ni} \underset{2° \text{ amine}}{RNHCH_3}$

12. (d) :



13. (d)

14. (a): Hydrolysis of methyl chloride to methanol follows S_N2 reaction. In contrast to polar protic solvents, which decrease the rate of S_N2 reaction by lowering the ground state energy of nucleophile, the polar aprotic solvents (DMF) increase the rate of S_N2 reactions by raising the ground state energy of nucleophile.

15. (b)

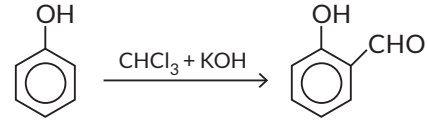
16. (d): Alcohols undergo intermolecular H-bonding and hence, their boiling points are higher than those of hydrocarbons.

17. (a) The phenoxide ion formed after loss of proton from phenol is resonance stabilised and thus phenol loses H^+ ion to show acidic character.

$$C_6H_5OH \longrightarrow \underset{\text{Resonance stabilised}}{C_6H_5O^-} + H^+$$

On the other hand alkoxide ion (formed from hexanol) shows no such resonance stabilisation and is unstable.

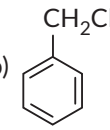
(b)



18. An aqueous $CuSO_4$ solution has $[Cu(H_2O)_4]^{2+}$ as the coordination entity which is of blue colour. The blue colour of $[Cu(H_2O)_4]^{2+}$ ions changes to green by the addition of F^- or Cl^- ions because both F^- and Cl^- ions are weaker ligands than H_2O. These ions create small splitting (Δ), *i.e.*, low energy light is required for small splitting. Thus light of red colour is absorbed and the $[CuF_4]^{2-}$ or $[CuCl_4]^{2-}$ complexes look green.

$[Cu(H_2O)_4]^{2+} + 4F^- \rightarrow [CuF_4]^{2-} + 4H_2O$

$[Cu(H_2O)_4]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 4H_2O$

19. (i) (a) (b) 

(ii) Order of increasing S_N2 reactivity :
$CH_3Br > CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl$

20. (i) $2CH_3CHO \xrightarrow{NaOH} \underset{\text{Aldol product}}{CH_3 - CH(OH) - CH_2 - CHO}$

(ii) $\underset{(A)}{CH_3COCH_3} \xrightarrow[C_2H_5ONa]{NH_2NH_2} \underset{\text{(Wolff-Kishner reduction)}}{CH_3CH_2CH_3}$

21. In solution, $x_A = 0{\cdot}30, \quad \therefore x_B = 0.70$
In the vapour phase, $y_A = 0.60 \quad \therefore y_B = 0.40$

But $y_A = \dfrac{P_A}{\text{TotalV.P.}} = \dfrac{P_A}{P_A + P_B} = \dfrac{x_A p°_A}{x_A p°_A + x_B p°_B}$

$$= \frac{0{\cdot}30p^\circ_A}{0{\cdot}30p^\circ_A + 0{\cdot}70p^\circ_B} = 0{\cdot}60 \qquad \text{...(i)}$$

$$y_B = \frac{p_B}{p_A + p_B} = \frac{x_B p°_B}{x_A p°_A + x_B p°_B} = \frac{0{\cdot}70p°_B}{0{\cdot}30p°_A + 0{\cdot}70p°_B} \qquad \text{...(ii)}$$

$= 0{\cdot}40$

Dividing eqn. (i) by eqn. (ii),

$$\frac{0{\cdot}30p°_A}{0{\cdot}70p°_B} = \frac{0{\cdot}60}{0{\cdot}40} \text{ or } \frac{p°_A}{p°_B} = \frac{0{\cdot}60}{0{\cdot}40} \times \frac{0{\cdot}70}{0{\cdot}30} = 3{\cdot}5$$

OR

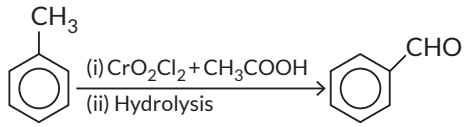
When the vapour pressure of a non-ideal solution is either higher or lower than that predicted by Raoult's law, the solution exhibits deviation.

These deviation are caused because of unequal intermolecular attractive force between solute-solvent molecules and solute-solute or solvent-solvent molecules.

Examples of positive deviation : Mixture of ethanol and acetone, carbon disulphide and acetone.

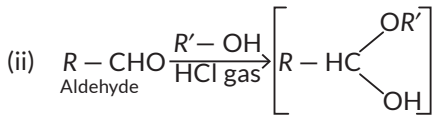
Examples of negative deviation : Chloroform and acetone, nitric acid and water.

22. (a) (i)

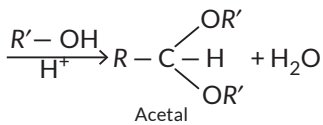


Toluene Benzaldehyde

(ii)



Aldehyde



Acetal

(b) $CH \equiv CH \xrightarrow[H_2SO_4 + HgSO_4]{H_2O} CH_3CHO \xrightarrow{[O]} CH_3COOH$

Acetylene Acetic acid

23. (a) Lead storage battery is a secondary cell.

Cell reactions

At anode : $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

At cathode : $PbO_{2(s)} + SO^{2-}{}_{4\,(aq)} + 4H^+ + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Overall cell reaction :

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

(b). Corrosion is a redox reaction by which metals are oxidised by oxygen in presence of moisture.

At anode : $2Fe \rightarrow 2Fe^{2+} + 4e^-$

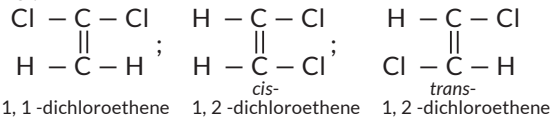
At cathode : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Overall reaction : $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$

The ferrous ions further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3.xH_2O$) and with further production of hydrogen ions.

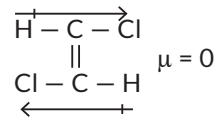
24. (a) Reaction of optically active 2-iodobutane with NaI in acetone (S_N1) leads to the formation of equal amounts of the two enantiomers. Thus product, being a racemic mixture, will be optically inactive.

(b) Dichloroethene exists in following three isomeric forms :



1, 1 -dichloroethene ; *cis*- 1, 2 -dichloroethene ; *trans*- 1, 2 -dichloroethene

The resultant dipole moment will be zero in case of *trans*-1, 2-dichloroethene.



(c) In the given sequence the increase in size (iodine atom being largest) and molecular weights are responsible for greater van der Waals' forces of attraction which overshadows the dipole-dipole attractions.

25. (i) The strength of the ligands in the spectrochemical series follows the order (increasing Δ_o value)

$H_2O < NH_3 < NO_2^-$

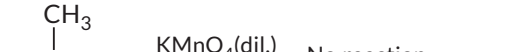
As $\Delta_o = \frac{hc}{\lambda}$, the order of wavelength absorbed is

$[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$

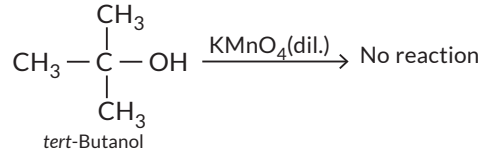
(ii) Ethane-1,2-diamine is stronger ligand than H_2O. When H_2O molecule is replaced by ethane-1,2-diamine (*en*), the crystal field splitting energy (Δ_o) increases. Complex absorbs light of higher frequency for *d-d* transition and hence colour of the complex changes from green to violet.

$$\underset{\text{small } \Delta_o}{[Ni(H_2O)_6]^{2+}} - \text{Green}, \quad \underset{\text{large } \Delta_o}{[Ni(en)_3]^{2+}} - \text{violet}$$

26.



n-Butanol Brown precipitate



tert-Butanol

This is because 3° alcohols do not undergo oxidation reaction.

OR

$C_2H_5OH \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} C_2H_4$

Ethyl alcohol (*A*) Ethylene (*B*)

$C_2H_4 + [O] + H_2O \xrightarrow{\text{alk.KMnO}_4} \underset{CH_2OH}{\overset{CH_2OH}{|}}$

(*B*)

$C_2H_4 + Br_2 \rightarrow BrCH_2 - CH_2Br$

$C_2H_4 + H_2 \xrightarrow[\text{High temperature}]{Ni} C_2H_6$

1 mole 1 mole

A is ethyl alcohol and *B* is ethylene.

27. (i) The value of (*i*) for dilute solution of glucose is 1 as it neither undergo association nor dissociation.

(ii) $\because \pi = CRT = \frac{w}{M \times V} \times RT = \frac{7.45}{74.5 \times 1} \times 0.0821 \times 300$

$= 2.463$

$\because$ (1000 mL = 1 litre)

Now $\underset{1}{KCl} \rightleftharpoons \underset{0}{K^+} + \underset{0}{Cl^-}$

$\underset{1-\alpha}{} \quad \underset{\alpha}{} \quad \underset{\alpha}{}$

Total moles $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{\pi_{obs}}{\pi_{cal}} = \frac{4.68}{2.463} = 1 + \alpha$$

$\therefore \quad \alpha = 0.90 = 90\%$

28. At 27°C, $T_1 = 273 + 27 = 300$ K, $(t_{1/2})_1 = 30$ min
At 47°C, $T_2 = 273 + 47 = 320$ K, $(t_{1/2})_2 = 10$ min

$$\therefore \quad k_2 = \frac{0.693}{10\,\text{min}} \text{ and } k_1 = \frac{0.693}{30\text{min}}$$

$$\text{or,} \quad \frac{k_2}{k_1} = \frac{0.693}{10\,\text{min}} \times \frac{30\,\text{min}}{0.693} = \frac{3}{1}$$

Using Arrhenius equation

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_2 \times T_1}\right]$$

$$\text{or,} \quad \log\frac{3}{1} = \frac{E_a}{2.303R}\left[\frac{320 - 300}{320 \times 300}\right]$$

$$\text{or,} \quad 0.4774 = \frac{E_a}{2.303 \times 8.314\,\text{JK}^{-1}\text{mol}^{-1}} \times \frac{20}{96000}$$

or $E_a = 0.4774 \times 19.147\ \text{J K}^{-1}\ \text{mol}^{-1} \times 4800\ \text{K}$
$= 43876\ \text{J mol}^{-1} = 43.876\ \text{kJ mol}^{-1}$

29. (a) Benzenesulphonyl chloride

(b) A primary amine forms *N*-alkylbenzene sulphonamide which because of the presence of an acidic hydrogen on the N-atom dissolves in aqueous KOH.

(c) A secondary amine forms *N,N*-dialkylbenzene sulphonamide which due to absence of acidic hydrogen on N-atoms does not dissolve in aqueous KOH.

OR

Tertiary amine does not contain a replaceable hydrogen on the nitrogen atom. So, 3° amine does not react with Hinsberg's reagent.

30. (a) The minimum extra energy which must be supplied to the reactants to enable them to cross over the potential energy barrier between reactants and products is called activation energy. It is denoted by E_a.

$E_a = E_T - E_R$

OR

(i) A catalyst lowers the activation energy (E_a) by providing an alternate pathway or reaction mechanism.

(ii) Catalyst does not affect the Gibbs energy (ΔG) of a reaction.

(b) The highly unstable transition state between reactants and products is called activated complex.

$$\underset{\text{Reactant}}{A + B} \rightarrow \underset{\text{Activated complex}}{AB} \rightarrow \text{Product}$$

Energy of activation = Energy of activated complex
– Average energy of reactants.

(c) For first order reaction, $t_{1/2} = \frac{0.693}{k}$

$$t_{1/2} = 200\text{min} = 200 \times 60 = 12000\,\text{s}$$

$$\Rightarrow \quad k = \frac{0.693}{12000\,\text{s}} = 5.8 \times 10^{-5}\,\text{s}^{-1}$$

Also, for first order decomposition of H_2O_2, rate constant is

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T}\text{K}$$

Comparing the above equation with the Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\Rightarrow \quad E_a = 2.303 \times 8.314 \times 1.0 \times 10^4$$
$$= 1.91 \times 10^5\ \text{J mol}^{-1}$$

31. (a) Amylose is a long straight chain with 200 - 1000 α-*D* (+) glucose units held by C_1 - C_4 glycosidic linkage. Amylopectin is branched chain polymer of α-*D*-glucose units in which chain is formed by C_1 - C_4 glycosidic linkage whereas branching occurs by C_1 - C_6 linkage.

(b) Aspartic acid. It has two – COOH groups and only one – NH_2 group, hence it is acidic amino acid.

(c) Riboflavin. Digestive disorders and cheilosis.

(d) T A G C A G G T

(e) Deoxyribose sugar, phosphoric acid and nitrogen containing heterocyclic bases are the hydrolysis products of DNA.

(f) During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact.

(g) (i) In diluted alkaline solution fructose undergoes isomerisation to glucose via mannose. This is why fructose reduces Tollens' reagent and Fehling solution although it contains a keto group.

32. (a) The given cell may be represented as

$Cu_{(s)}|Cu^{2+}| \,|Cl_{2(g)}|Cl^-$

(i) $E^\circ_{cell} = E^\circ_c - E^\circ_a = (+1.36\text{V}) - (+0.34\text{V}) = 1.02\ \text{V}$

(ii) $\Delta_r G^\circ = -nFE^\circ = -2 \times 96500\text{C} \times 1.02\text{V} = 196.86\ \text{kJ}$

(iii) $E^\circ_{cell} = \frac{0.0591}{n}\log K$

$$K = \text{antilog}\frac{2 \times 1.02\,\text{V}}{0.0591} = \text{antilog (34.51)}$$

$K = 3.236 \times 10^{34}$

(b) The given cell may be represented as

Pt, H_2 (1 atm) | H^+ (pH = ?) | | H^+ (pH = 1) | H_2 (1 atm)

Using formula, $E_{cell} = \frac{0.0591}{1}\log\frac{[H^+]_c}{[H^+]_a}$

or, $0.16\ \text{V} = 0.0591\ \text{V}\,[\log [H^+]_c - \log [H^+]_a]$

or, $0.16\ \text{V} = 0.0591\ \text{V}\,[pH_a - pH_c]$

$0.16\ \text{V} = 0.0591\ [pH_a - 1]$

$$\text{or,} \quad pH_a - 1 = \frac{0.16}{0.0591} = 2.70$$

or, $pH_a = 2.70 + 1 = 3.70$

OR

(a) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.403 - (-0.763) = 0.36$ V

The net cell reaction is

$Zn_{(s)} + Cd^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cd_{(s)}$

Here, value of $n = 2$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cd^{2+}]}$$

$$= 0.36 - \frac{0.0591}{2}\log\frac{0.0004}{0.2}$$

$$= 0.36 - \frac{0.0591}{2}(-2.69) = 0.36 + 0.08 = 0.44 \text{ V}$$

$\therefore \quad \Delta G = -nFE_{cell} = -2 \times 96500 \times 0.44$

$= -84920$ J/mol

(b) $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

$$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{0.059}{2}\log\frac{[Cu]}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.059}{2}\log\frac{1}{0.1} = 0.34 - \frac{0.059}{2}\log 10$$

$$= 0.34 - \frac{0.059}{2} \times (1) = 0.34 - 0.0295 = 0.3105 \text{ V}$$

When the concentration of Cu^{2+} ions is decreased, the potential for copper electrode decreases.

33. (a) (i) The ionic species which possesses unpaired electron or electrons in $(n-1)d$-subshell will show colour. Out of the ions $Ag^+(4d^{10})$, $Co^{2+}(3d^7)$ and $Ti^{4+}(3d^0)$, Co^{2+} will be coloured as it contains three unpaired electrons, Ag^+ and Ti^{4+} will be colourless.

(ii) When placed in magnetic field, Co^{2+} will be attracted because it is paramagnetic due to unpaired electrons. Ag^+ and Ti^{4+} ions will be repelled by the magnetic field as they are diamagnetic.

(b) (i) Na_2SO_3 is a reducing agent. It reduced acidified $K_2Cr_2O_7$ to chromic sulphate which is green in colour.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3Na_2SO_3 \longrightarrow K_2SO_4 + 3Na_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + 4H_2O$$

(ii) Ferrous salt acts as a reducing agent. It reduces acidified $KMnO_4$ into $MnSO_4$ and K_2SO_4 which form colourless solution, *i.e.*, decolourisation of $KMnO_4$ solution takes place.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

OR

(a) (i) $\underset{\text{Sod. chromate}}{2Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{Sod. dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$

$$\underset{\text{Sod. dichromate}}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{\text{Pot. dichromate}}{K_2Cr_2O_7} + 2NaCl$$

(ii) The potassium manganate is oxidised to potassium permanganate by oxidation with chlorine.

$2K_2MnO_{4(aq)} + Cl_{2(g)} \rightarrow 2KMnO_{4(aq)} + 2KCl_{(g)}$

(b) The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

It is caused due to imperfect shielding of nuclear charge by 4*f*-electrons.

Lanthanum (La) has the largest ionic radius while lutetium (Lu) has the smallest among the 4*f*-series elements.

Consequences of lanthanoid contraction :

(i) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(ii) Lanthanum hydroxide $La(OH)_3$ is most basic and lutetium hydroxide $Lu(OH)_3$ is least basic.

(iii) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar. *e.g.* Atomic radii of zirconium (Zr) is same as that of hafnium (Hf).

CBSE SAMPLE PAPER 2023-24

(Based on CBSE Circular released on 31st March 2023)

General Instructions :

Read the following instructions carefully.

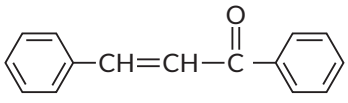
(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple -choice questions carrying 1 mark each.
(c) SECTION B consists of 5 short answer questions carrying 2 marks each.
(d) SECTION C consists of 7 short answer questions carrying 3 marks each.
(e) SECTION D consists of 2 case - based questions carrying 4 marks each.
(f) SECTION E consists of 3 long answer questions carrying 5 marks each.
(g) All questions are compulsory.
(h) Use of log tables and calculators is not allowed.

Time allowed : 3 hours **Maximum marks :** 70

SECTION - A

The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Which of the following solutions will have the highest conductivity at 298 K?
   (a) 0.01 M HCl solution
   (b) 0.1 M HCl solution
   (c) 0.01 M CH_3COOH solution
   (d) 0.1 M CH_3COOH solution

2. $A + B \xrightarrow{\text{dil. NaOH}}$ 

   Identify *A* and *B* :
   (a) *A* = 1-phenylethanal, *B* = acetophenone
   (b) *A* = Benzophenone, *B* = formaldehyde
   (c) *A* = Benzaldehyde, *B* = Acetophenone
   (d) *A* = Benzophenone, *B* = Acetophenone

3. The vitamins which can be stored in our body are
   (a) Vitamin A, B, D and E
   (b) Vitamin A, C, D and K
   (c) Vitamin A, B, C and D
   (d) Vitamin A, D, E and K

4. What is IUPAC name of the ketone *A*, which undergoes iodoform reaction to give $CH_3CH{=}C(CH_3)COONa$ and yellow precipitate of CHI_3?
   (a) 3-Methylpent-3-en-2-one
   (b) 3-Methylbut-2-en-one
   (c) 2, 3-Dimethylethanone
   (d) 3-Methylpent-4-one

5. Which of the following is not correct?
   (a) In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring.
   (b) The carbon-magnesium bond is covalent and non-polar in nature.
   (c) During S_N1 reaction, the carbocation formed in the slow step being sp^2 hybridised is planar.
   (d) Out of $CH_2{=}CH{-}Cl$ and $C_6H_5CH_2Cl$, $C_6H_5CH_2Cl$ is more reactive towards S_N1 reaction.

6. Match the properties with the elements of 3*d* series:

(i)	Lowest enthalpy of atomisation	(p)	Sc
(ii)	Shows maximum number of oxidation states	(q)	Mn
(iii)	Transition metal that does not form coloured compounds	(r)	Zn
		(s)	Ti

   (a) (i)-(r), (ii)-(q), (iii)-(p) (b) (i)-(r), (ii)-(s), (iii)-(p)
   (c) (i)-(p), (ii)-(q), (iii)-(r) (d) (i)-(s), (ii)-(r), (iii)-(p)

7. Which of the following statement is true?
   (a) Molecularity of reaction can be zero or a fraction.
   (b) Molecularity has no meaning for complex reactions.
   (c) Molecularity of a reaction is an experimental quantity
   (d) Reactions with the molecularity three are very rare but are fast.

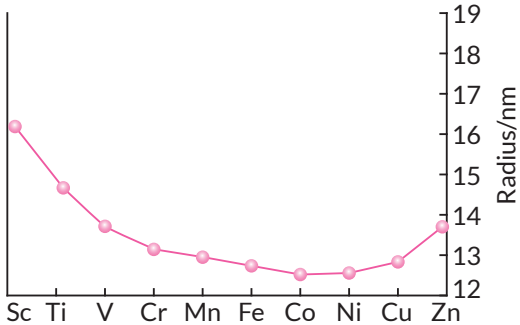
8. In which of the following solvents, the $C_4H_8NH_3^+X^-$ is soluble?
   (a) Ether (b) Acetone
   (c) Water (d) Bromine water

9. Which of the following observation is shown by 2-phenyl ethanol with Lucas reagent?
   (a) Turbidity will be observed within five minutes.
   (b) No turbidity will be observed.
   (c) Turbidity will be observed immediately.
   (d) Turbidity will be observed at room temperature but will disappear after five minutes.

10. If the initial concentration of substance *A* is 1.5 M and after 120 seconds the concentration of substance *A* is 0.75 M, the rate constant for the reaction if it follows zero - order kinetics is
(a) 0.00625 mol $L^{-1}s^{-1}$ (b) 0.00625 s^{-1}
(c) 0.00578 mol $L^{-1}s^{-1}$ (d) 0.00578 s^{-1}

11. Anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst
(a) due to the activation of benzene ring by the methoxy group.
(b) due to the de-activation of benzene ring by the methoxy group.
(c) due to the increase in electron density at *ortho* and *para* positions
(d) due to the formation of stable carbocation .

12. The trend of which property is represented by the following graph?



(a) Ionization Enthalpy
(b) Atomic Radii
(c) Enthalpy of atomization
(d) Melting point

13. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Alcohols react both as nucleophiles and electrophiles.
Reason (R) : The bond between C–O is broken when alcohols react as nucleophiles.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

14. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : Strong oxidising agents oxidise toluene and its derivatives to benzoic acids.
Reason (R) : It is possible to stop the oxidation of toluene at the aldehyde stage with suitable reagents.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

15. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion : Enzymes are very specific for a particular reaction and for a particular substrate.
Reason : Enzymes are biocatalysts.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : During electrolysis of aqueous copper sulphate solution using copper electrodes hydrogen gas is released at the cathode.
Reason (R) : The electrode potential of Cu^{2+}/Cu is greater than that of H^+/H_2.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION - B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17. (a) Radioactive decay follows first - order kinetics. The initial amount of two radioactive elements *X* and *Y* is 1 g each. What will be the ratio of *X* and *Y* after two days if their half-lives are 12 hours and 16 hours respectively?
(b) The hypothetical reaction, $P + Q \rightarrow R$ is half order *w.r.t.* '*P*' and zero order *w.r.t.* '*Q*'. What is the unit of rate constant for this reaction?

18. A 5% solution of $Na_2SO_4 \cdot 10H_2O$ (*M.W* = 322) is isotonic with 2% solution of non-electrolytic, non volatile substance *X*. Find out the molecular weight of *X*.

19. (a) Arrange the isomeric dichlorobenzene in the increasing order of their boiling point and melting points.

(b) Explain why the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

20. (a) Out of *p*-tolualdehyde and *p*-nitrobenzaldehyde, which one is more reactive towards nucleophilic addition reactions, why?

(b) Write the structure of the product formed when acetone reacts with 2,4-DNP reagent.

OR

Convert the following:

(a) Benzene to *m*-nitrobenzaldehyde

(b) Bromobenzene to benzoic acid

21. (a) DNA fingerprinting is used to determine paternity of an individual. Which property of DNA helps in the procedure?

(b) What structural change will occur when a native protein is subjected to change in pH?

SECTION - C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. (a) Write the formula for the following coordination compound: *Bis*(ethane-1,2-diamine)dihydroxidochromium(III) chloride

(b) Does ionization isomer for the following compound exist? Justify your answer. $Hg[Co(SCN)_4]$

(c) Is the central metal atom in coordination complexes a Lewis acid or a Lewis base? Explain.

23. (a) Can we construct an electrochemical cell with two half-cells composed of $ZnSO_4$ solution and zinc electrodes? Explain your answer.

(b) Calculate the λ°_m for Cl^- ion from the data given below:

$\Lambda^\circ_m\ MgCl_2 = 258.6\ S\ cm^2\ mol^{-1}$ and $\lambda^\circ_m\ Mg^{2+} = 106\ S\ cm^2\ mol^{-1}$

(c) The cell constant of a conductivity cell is 0.146 cm^{-1}. What is the conductivity of 0.01 M solution of an electrolyte at 298 K, if the resistance of the cell is 1000 ohm?

24. Write the name of the reaction, structure and IUPAC name of the product formed when

(a) phenol reacts with $CHCl_3$ in the presence of NaOH followed by hydrolysis.

(b) $CH_3CH_2CH(CH_3)CH(CH_3)ONa$ reacts with C_2H_5Br.

25. You are given four organic compounds "*A*", "*B*", "*C*" and "*D*". The compounds "*A*", "*B*" and "*C*" form an orange-red precipitate with 2,4-DNP reagent. Compounds "*A*" and "*B*" reduce Tollens' reagent while compounds "*C*" and "*D*" do not. Both "*B*" and "*C*" give a yellow precipitate when heated with iodine in the presence of NaOH. Compound "*D*" gives brisk effervescence with sodium bicarbonate solution. Identify "*A*", "*B*", "*C*" and "*D*" given the number of carbon atoms in three of these carbon compounds is three while one has two carbon atoms. Give an explanation for your answer.

26. When sucrose is hydrolysed the optical rotation values are measured using a polarimeter and are given in the following table:

S.No.	Time (hours)	Specific Rotation
1	0	+ 66.5°
2	∞	–39.9°

(a) Account for the two specific rotation values.

(b) What is the specific name given to sucrose based on the above observation .

(c) One of the products formed during the hydrolysis of sucrose is a glucose, that reacts with hydroxylamine to give compound *A*. Identify compound *A*.

27. An organic compound *A* with the molecular formula, $(+)C_4H_9Br$ undergoes hydrolysis to form $(\pm)\ C_4H_9OH$. Give the structure of *A* and write the mechanism of the reaction.

28. The rate constants of a reaction at 200 K and 500 K are 0.02 s^{-1} and 0.20 s^{-1} respectively. Calculate the value of E_a (Given; 2.303 R = 19.15 J K^{-1} mol^{-1})

SECTION - D

The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29. Crystal field splitting by various ligands

Metal complexes show different colours due to *d-d* transitions. The complex absorbs light of specific wavelength to promote the electron from t_{2g} to e_g level. The colour of the complex is due to the transmitted light, which is complementary of the colour absorbed.

The wave number of light absorbed by different complexes of Cr ion are given below:

Complex	Wavenumber of light absorbed (cm^{-1})	Energy of light absorbed (kJ/mol)
$[CrA_6]^{3-}$	13640	163
$[CrB_6]^{3+}$	17830	213
$[CrC_6]^{3+}$	21680	259
$[CrD_6]^{3-}$	26280	314

Answer the following questions:

(a) Out of the ligands "*A*", "*B*", "*C*" and "*D*", which ligand causes maximum crystal field splitting? Why?

OR

Which of the two, "*A*" or "*D*" will be a weak field ligand? Why?

(b) Which of the complexes will be violet in colour? $[CrA_6]^{3-}$ or $[CrB_6]^{3+}$ and why?
(Given: If 560-570 nm of light is absorbed, the colour of the complex observed is violet.)

(c) If the ligands attached to Cr^{3+} ion in the complexes given in the table above are water, cyanide ion, chloride ion, and ammonia (not in this order)

Identify the ligand, write the formula and IUPAC name of the following :

(i) $[CrA_6]^{3-}$

(ii) $[CrC_6]^{3+}$

30. The lead-acid battery represents the oldest rechargeable battery technology. Lead acid batteries can be found in a wide variety of applications including small-scale power storage such as UPS systems, ignition power sources for automobiles, along with large, grid-scale power systems. The spongy lead act as the anode and lead dioxide as the cathode. Aqueous sulphuric acid is used as an electrolyte. The half-reactions during discharging of lead storage cells are:

Anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{(s)} + 2e^-$

Cathode : $PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O$

There is no safe way of disposal and these batteries end-up in landfills. Lead and sulphuric acid are extremely hazardous and pollute soil, water as well as air. Irrespective of the environmental challenges it posses, lead-acid batteries have remained an important source of energy.

Designing green and sustainable battery systems as alternatives to conventional means remains relevant. Fuel cells are seen as the future source of energy. Hydrogen is considered a green fuel. Problem with fuel cells at present is the storage of hydrogen. Currently, ammonia and methanol are being used as a source of hydrogen for fuel cell. These are obtained industrially, so add to the environmental issues.

If the problem of storage of hydrogen is overcome, is it still a "green fuel?" Despite being the most abundant element in the Universe, hydrogen does not exist on its own so needs to be extracted from the water using electrolysis or separated from carbon fossil fuels. Both of these processes require a significant amount of energy which is currently more than that gained from the hydrogen itself. In addition, this extraction typically requires the use of fossil fuels. More research is being conducted in this field to solve these problems. Despite the problem of no good means to extract hydrogen, it is a uniquely abundant and renewable source of energy, perfect for our future zero-carbon needs.

Answer the following questions :

(a) How many coulombs have been transferred from anode to cathode in order to consume one mole of sulphuric acid during the discharging of lead storage cell?

(b) How much work can be extracted by using lead storage cell if each cell delivers about 2.0 V of voltage? (1 F = 96500 C)

(c) Do you agree with the statement – "Hydrogen is a green fuel." Give your comments for and against this statement and justify your views.

OR

Imagine you are a member of an agency funding scientific research. Which of the following projects will you fund and why?

(i) Safe recycling of lead batteries

(ii) Extraction of hydrogen

SECTION - E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31. Attempt **any five** of the following:

(a) Which of the following ions will have a magnetic moment value of 1.73 B.M.

Sc^{3+}, Ti^{3+}, Ti^{2+}, Cu^{2+}, Zn^{2+}

(b) In order to protect iron from corrosion, which one will you prefer as a sacrificial electrode, Ni or Zn? Why? (Given: standard electrode potentials of Ni, Fe and Zn are –0.25 V, –0.44 V and –0.76 V respectively.)

(c) The second ionization enthalpies of chromium and manganese are 1592 and 1509 kJ/mol respectively. Explain the lower value of Mn.

(d) Give two similarities in the properties of Sc and Zn.

(e) What is actinoid contraction? What causes actinoid contraction?

(f) What is the oxidation state of chromium in chromate ion and dichromate ion?

(g) Write the ionic equation for reaction of KI with acidified $KMnO_4$.

32. (a) What is the effect of temperature on the solubility of glucose in water?

(b) Ibrahim collected a 10 mL each of fresh water and ocean water. He observed that one sample labeled "*P*" froze at 0 °C while the other "*Q*"

at −1.3 °C. Ibrahim forgot which of the two, "*P*" or "*Q*" was ocean water. Help him identify which container contains ocean water, giving rationalization for your answer.

(c) Calculate van't Hoff factor for an aqueous solution of $K_3[Fe(CN)_6]$ if the degree of dissociation (α) is 0.852. What will be boiling point of this solution if its concentration is 1 molal? (K_b=0.52 K kg/mol)

OR

(a) What type of deviation from Raoult's Law is expected when phenol and aniline are mixed with each other? What change in the net volume of the mixture is expected? Graphically represent the deviation.

(b) The vapour pressure of pure water at a certain temperature is 23.80 mm Hg. If 1 mole of a non-volatile non-electrolytic solute is dissolved in 100 g water, Calculate the resultant vapour pressure of the solution.

33. An organic compound with molecular formula $C_7H_7NO_2$ exists in three isomeric forms, the isomer '*A*' has the highest melting point of the three. '*A*' on reduction gives compound '*B*' with molecular formula C_7H_9N. '*B*' on treatment with $NaNO_2$/HCl at 0-5 °C to form compound '*C*'. On treating *C* with H_3PO_2,it gets converted to *D* with formula C_7H_8, which on further reaction with CrO_2Cl_2 followed by hydrolysis forms '*E*' C_7H_6O . Write the structure of compounds *A* to *E*. Write the chemical equations involved.

(a) Account for the following:

(i) *N*-ethylbenzenesulphonyl amide is soluble in alkali .

(ii) Reduction of nitrobenzene using Fe and HCl is preferred over Sn and HCl.

(b) Arrange the following in

(i) decreasing order of pK_b values
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$, CH_3NH_2, NH_3

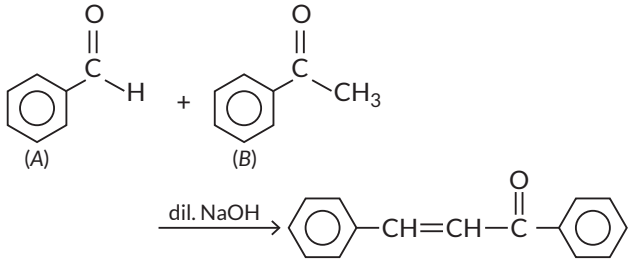
(ii) increasing order of solubility in water
C_2H_5Cl, $C_2H_5NH_2$, C_2H_5OH

(iii) decreasing boiling point
CH_3COOH, C_2H_5OH, CH_3NH_2, CH_3OCH_3

Detailed SOLUTIONS

1. (b): Among the given solutions 0.1 M HCl solution has highest conductivity at 298 K since HCl is strong electrolyte and conductivity is higher for strong electrolytes, also conductivity decreases with dilution.

2. (c): *A* = Benzaldehyde, *B* = Acetophenone. This is an example of crossed Aldol condensation.



3. (d): Vitamins A, D, E and K are fat soluble vitamins which can be stored in our body.

4. (a): $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH-CH_3$
3-Methylpent-3-en-2-one

The compounds which give haloform reactions contain CH_3CO- group or $CH_3CH(OH)-$group.

Among the given compounds, 3-methylpent-3-en-2-one gives iodoform reaction.

$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH-CH_3 + 3NaOI \longrightarrow CH_3CH=C(CH_3)COONa + CHI_3$$

5. (b): In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar with carbon pulling electrons from electropositive magnesium, the magnesium halogen bond is essentially ionic, $\overset{\delta-}{R}-\overset{\delta+}{Mg}X$.

6. (a): Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence are not regarded as transition metals.

Thus, Zinc has no unpaired electrons in 3*d* or 4*s* orbitals, so enthalpy of atomization is low.

Mn = $3d^5 4s^2$ shows +2, +3, +4, +5, +6 and +7 oxidation state, maximum number of oxidation state.

Sc exists in the oxidation state (+3) and as a result the ions and their compounds are colourless and diamagnetic.

(i)-(r) , (ii)-(q), (iii)-(p)

7. (b): Molecularity cannot be zero or a non-integer. Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. Molecularity is a theoretical concept. Reactions with the molecularity three are very rare and slow to proceed.

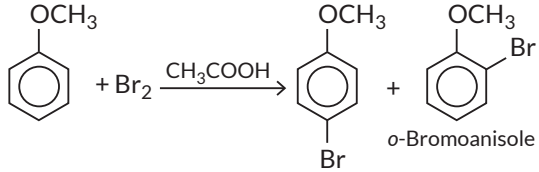
8. (c): Amine salts are soluble in water but are insoluble in non-polar solvents such as benzene, ether, acetone, chloroform, etc.

9. (b): With Lucas reagent, no turbidity will be observed, so given compound is a primary alcohol.

10. (a): For zero order reaction,

$$k = \frac{[R]_0 - [R]}{t} = \frac{1.5 - 0.75}{120} = 0.00625 \text{ mol L}^{-1} \text{ s}^{-1}$$

11. (a): An Anisole undergoes bromination with Br_2, even in the absence of $FeBr_3$ due to the activation of benzene ring by the methoxy group.



12. (b): Atomic and ionic radii of transition metals show progressive decrease with increasing atomic number.

13. (c): When alcohol react as nucleophiles the bond between O—H is broken so, reason is false.

14. (b): Both A and R are true but R is not the correct explanation of A.

15. (b): Both A and R are true but R is not the correct explanation of A.

16. (d): Cu will deposit at cathode so, A is false but R is true.

17. (a): For first order reaction,
Half-life of X = 12 hours
2 days = 48 hours means 4 half lives,
Amount of X left = 1/16 of initial value
Half-life of Y = 16 hours
2 days = 48 hours means 3 half lives,
Amount left = 1/8 of initial value.
Ratio of $X : Y$ = 1:2
(b) $mol^{1/2}L^{-1/2}s^{-1}$ as, Rate = $k\,[P]^{1/2}$

18. $\underset{(Na_2SO_4)}{\pi_1} = \underset{\text{(Non-electrolytic solution)}}{\pi_2}$

$iC_1RT = C_2RT$, (i = 3, for Na_2SO_4)

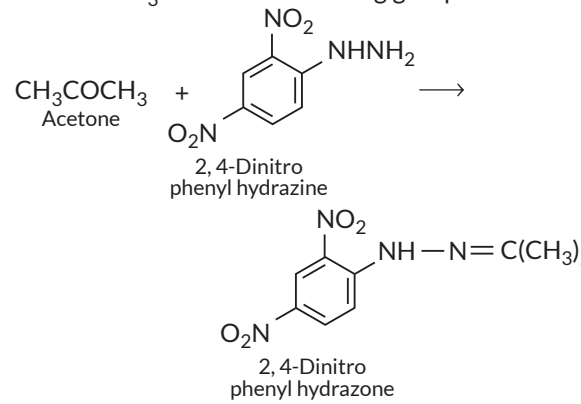
$$\frac{3 \times 5}{322} = \frac{2}{M}$$

$$M = \frac{2 \times 322}{3 \times 5} = 42.9 \text{ g}$$

19. (a) *m*-Dichlorobenzene < *o*-Dichlorobenzene < *p*-Dichlorobenzene
Para isomers are symmetrical and fits the crystal lattice in better way.
Ortho has a stronger dipole dipole interaction as compared to *meta* is omer.
(b) The halogen atom because of its $-I$ effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

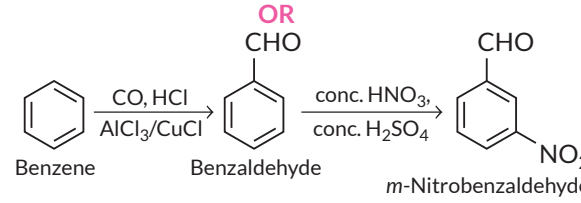
20. (a) *p*-Nitrobenzaldehyde is more reactive towards the nucleophilic addition reaction than *p*- tolualdehyde as nitro group is electron withdrawing in nature . Presence of nitro group decrease electron density, hence facilitates the attack of nucleophile . Presence of $-CH_3$ leads to $+I$ effect as $-CH_3$ is electron releasing group.

(b)

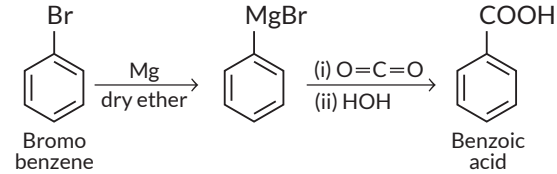


OR

(a)



(b)



21. (a) Replication ; A sequence of bases on DNA is unique for a person and is the genetic material transferred to the individual from the parent which helps in the determination of paternity.
(b) During denaturation secondary and tertiary structures are destroyed but the primary structure remains intact.

22. (a) $[Cr(en)_2(OH)_2]Cl$ or $[Cr(H_2NCH_2CH_2NH_2)_2(OH)_2]Cl$
(b) No, ionization isomers are possible by exchange of ligand with counter ion only and not by exchange of central metal ion.
(c) The central atom is electron pair acceptor so, it is a Lewis acid.

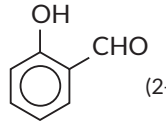
23. (a) Yes, if the concentration of $ZnSO_4$ in the two half cell is different , the electrode potential will be different making the cell possible.
(b) $\lambda^\circ_m (MgCl_2) = \lambda^\circ_m (Mg^{2+}) + 2\lambda^\circ_m (Cl^-)$
$258.6 = 106 + 2\lambda^\circ_m (Cl^-)$

$\lambda^{\circ}_m(Cl^-) = 76.3\ S\ cm^2\ mol^{-1}$

(c) Cell constant, $G^* = k \times R$

$k = G^*/R = 0.146/1000 = 1.46 \times 10^{-4}\ Scm^{-1}$.

24. (a) Reimer – Tiemann reaction



(2-Hydroxybenzaldehyde)

(b) Williamson synthesis,

$CH_3CH_2CH(CH_3)CH(CH_3)OC_2H_5$

(2- Ethoxy-3-methylpentane)

25. *A*, *B* and *C* contain carbonyl group as they give positive 2,4-DNP test. *A* and *B* are aldehydes as aldehydes reduce Tollens' reagent.

C is a ketone, as it contains carbonyl group but does not give positive Tollen's test.

C is a methyl ketone as it gives positive iodoform test.

B is an aldehyde that gives positive iodoform test.

D is a carboxylic acid. Since, the number of carbons in the compounds *A*, *B*, *C* and *D* is three or two.

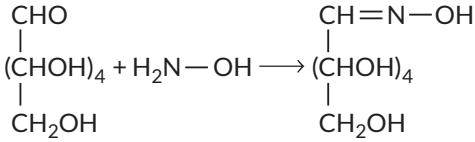
B is CH_3CHO as this is only aldehyde which gives a positive iodoform test.

The remaining compounds *A*, *C* and *D* have three carbons , *A* is CH_3CH_2CHO, *C* is CH_3COCH_3 and *D* is CH_3CH_2COOH.

26. (a) Sucrose is *dextro*-rotatory with a specific rotation of $[\alpha]_D = +66.5°$ but on hydrolysis, it gives *dextro*-rotatory glucose and *laevo*-rotatory fructose. Since, the *laevo*-rotation of fructose (–92.4°) is much more than *dextro*-rotation of glucose (+ 52.5°), therefore the resulting solution is *laevo*-rotatory.

(b) Invert sugar, the hydrolysis of sucrose brings about a change in the sign of rotation, from *dextro* (+) to *laevo* (–) and the product is named as invert sugar.

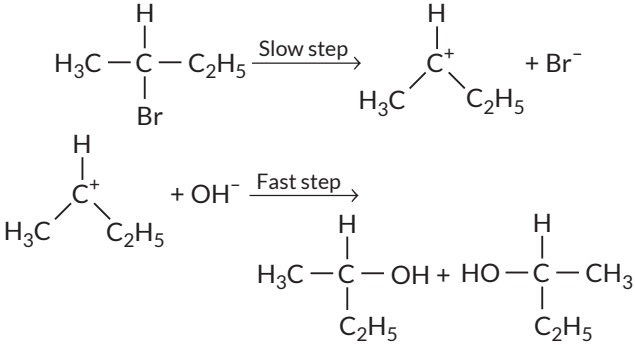
(c) Glucose reacts with hydroxylamine to form an oxime.



(*A*)

27. *A* is $C_2H_5-CH(Br)-CH_3$

Mechanism:



28. $$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{0.20}{0.02} = \frac{E_a}{2.303R}\left[\frac{1}{200} - \frac{1}{500}\right]$$

$$\log 10 = \frac{E_a}{19.15}\left(\frac{300}{200\times 500}\right)$$

$$E_a = \frac{19.15\times 200\times 500}{300}$$

$E_a = 6383$ J/mol

29. (a) *D* will cause maximum crystal field splitting. Energy is directly proportional to the wave number. Maximum energy of light is required for an electron to jump from t_{2g} to e_g in case of $[CrD_6]^{3-}$

OR

A will be weak field ligand. The splitting caused least in this case as the energy required for electron to jump from t_{2g} to e_g, is minimum.

(b) $[CrB_6]^{3+}$ will be violet in color, wavelength of light absorbed is 1/17830 = 560 nm for the complex while 1/13640 = 733 nm for $[CrA_6]^{3-}$ complex.

(c) (i) $[CrCl_6]^{3-}$, Hexachloridochromate(III) ion

(ii) $[Cr(NH_3)_6]^{3+}$, Hexaamminechromium(III) ion

A = Cl^-, *B* = H_2O, *C* = NH_3, *D* = CN^-

30. (a) 2 mol e^- (or 2F) have been transferred from anode to cathode to consume 2 mol of H_2SO_4 therefore, one mole H_2SO_4 requires one Faraday of electricity or 96500 coulombs.

(b) $W_{max} = -nFE° = -2\times 96500\times 2.0 = 386000$ J of work can be extracted using lead storage cell when the cell is in use.

(c) Both yes and no should be accepted as correct answers.

Yes, Hydrogen is a fuel that on combustion gives water as a byproduct. There are no carbon emissions and no pollutions caused.

However, at present the means to obtain hydrogen are electrolysis of water which use electricity obtained from fossil fuels and increase carbon emissions.

Inspite of the problems faced today in the extraction of hydrogen, we cannot disagree on the fact that hydrogen is a clean source of energy. Further research can help in finding solutions and greens ways like using solar energy for extraction of hydrogen.

No, It is true that hydrogen is a fuel that on combustion gives water as a byproduct. There are no carbon emissions and no pollutions caused.

However, at present the means to obtain hydrogen are electrolysis of water which use electricity obtained from fossil fuels and increase carbon emissions.

Hydrogen is no doubt a green fuel, but the process of extraction is not green as of today. At present, looking at the process of extraction, hydrogen is not a green fuel.

OR

Recycled lead batteries and hydrogen production both are a valuable commodity in the developing world.

(i) Lead batteries are currently the most important and widely used batteries. These are rechargeable. The problem is waste management which needs research and awareness. Currently, these are being thrown into landfills and there is no safe method of disposal or recycling. Research into safer method of disposal will reduce the pollution and health hazards caused to a great extent.

(ii) Fuel cell is a clean source of energy. Hydrogen undergoes combustion to produce water. The need of the hour is green fuel and hydrogen is a clean fuel. The current problem is obtaining hydrogen. Research that goes into this area will help solve the problem of pollution and will be a sustainable solution.

31. (a) Both Ti^{3+} and Cu^{2+} have 1 unpaired electron, so the magnetic moment for both will be 1.73 B.M.

(b) Zn, it has a more negative electrode potential so, will corrode itself in place of iron.

(c) Mn^{+} has $3d^5 4s^1$ configuration and configuration of Cr^{+} is $3d^5$, therefore, ionisation enthalpy of Mn^{+} is lower than Cr^{+}.

(d) Sc and Zn both form colourless compound and are diamagnetic.

(e) The decrease in the atomic and ionic radii with increase in atomic number of actinoids due to poor shielding effect of 5*f* electron.

(f) In both chromate and dichromate ion the oxidation state of Cr is +6.

(g) In acidic solution, iodine is liberated from potassium iodide :

$$10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

32. (a) Addition of glucose to water is an endothermic reaction. According to Le-Chatelier's principle, on increase in temperature, solubility will increase.

(b) *Q* is ocean water, due to the presence of salts it freezes at lower temperature (depression in freezing point).

(c) $K_3[Fe(CN)_6]$ gives 4 ions in aqueous solution,

$i = 1 + (n - 1)\alpha$

$i = 1 + (4 - 1) \times 0.852$

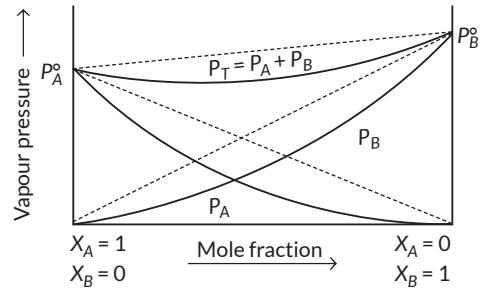
$i = 3.556$

$\Delta T_b = iK_b\, m = 3.556 \times 0.52 \times 1 = 1.85$

$T_b = 101.85°C$

OR

(a) Negative deviation is expected when phenol and aniline are mixed with each other. The net volume of the mixture will decrease, $\Delta V < 0$ due to stronger intermolecular interactions.



P-X Diagram for solutions showing negative deviation from Raoult's Law

(b) Relative lowering of vapour pressure

$= (P° - P) / P° = x_2$

$x_2 = n_2/n_1$

$n_2 = 0.1$

$n_1 = 100/18$

$x_2 = 0.1/ 5.55 + 0.1 = 0.1/ 5.65 = 0.018$

$P° = 23.80$ mm Hg

Relative lowering of vapour pressure

$= (23.80 - P) / 23.80 = 0.018$

$23.80 - P = 0.428$

$P = 23.80 - 0.428 = 23.37$ mm Hg

33. Compound *A* is *p*-methylnitrobenzene

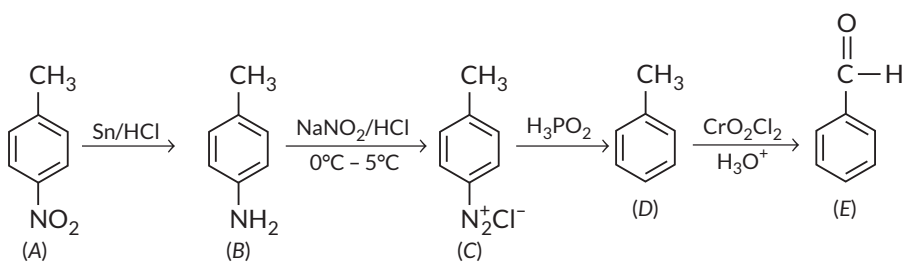
Compound *B* is *p*-methylbenzenamine

Compound *C* is *p*-methylbenzenediazoniumchloride

Compound *D* is Toluene

Compound *E* is Benzaldehyde

The chemical reactions involved are



OR

(a) (i) The hydrogen attached to *N*-ethylbenzene sulphonamide is acidic in nature. This is due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(ii) Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

(b) (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > NH_3 > C_6H_5CH_2NH_2 > CH_3NH_2$

(ii) $C_2H_5Cl < C_2H_5NH_2 < C_2H_5OH$

(iii) $CH_3COOH > C_2H_5OH > CH_3NH_2 > CH_3OCH_3$